REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

January 1960

● VOLUME 3

● NUMBER 1

TECHNICAL PROGRESS REVIEWS

To meet the needs of industry for concise summaries of current atomic developments, the Atomic Energy Commission is publishing this series, Technical Progress Reviews. Issued quarterly, each of the reviews digests and evaluates the latest findings in a specific area of nuclear technology and science.

The four journals published in this series are:

Nuclear Safety, W. B. Cottrell, editor, R. A. Charpie, advisory editor, and associates, Oak Ridge National Laboratory

Power Reactor Technology, Walter H. Zinn and associates, General Nuclear Engineering Corporation

Reactor Core Materials (covering solid material developments), R. W. Dayton, E. M. Simons, and associates, Battelle Memorial Institute

Reactor Fuel Processing, Stephen Lawroski and associates, Chemical Engineering Division, Argonne National Laboratory

Each journal may be purchased ($2.00 per year for subscription and individual issues $0.55) from the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C. See back cover for remittance instructions and foreign postage requirements.

●

Availability of Reports Cited in This Review

Unclassified AEC reports are available for inspection at AEC depository libraries and are sold by the Office of Technical Services, Department of Commerce, Washington 25, D. C.

Unclassified reports issued by other Government agencies or private organizations should be requested from the originator.

Unclassified British and Canadian reports may be inspected at AEC depository libraries. British reports are sold by the British Information Service, 45 Rockefeller Plaza, New York, N. Y.; Canadian reports (AECL series) are sold by the Scientific Document Distribution Office, Atomic Energy of Canada, Ltd., Chalk River, Ontario, Canada.

Classified U. S. and foreign reports identified in this journal as Secret or Confidential may be purchased by properly cleared Access Permit Holders from the Technical Information Service Extension, U. S. Atomic Energy Commission, P. O. Box 1001, Oak Ridge, Tenn. Such reports may be inspected at classified AEC depository libraries.

REACTOR
FUEL
PROCESSING

A REVIEW OF RECENT DEVELOPMENTS

Prepared for U. S. ATOMIC ENERGY COMMISSION
by ARGONNE NATIONAL LABORATORY

● JAN. 1960

● VOLUME 3

● NUMBER 1

foreword

This quarterly review of *Reactor Fuel Processing* has been prepared at the request of the U. S. Atomic Energy Commission, Division of Information Services. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this broad field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review who are personnel of the Argonne National Laboratory, Chemical Engineering Division. Those taking part in the preparation of this issue are L. Burris, Jr., A. A. Chilenskas, I. G. Dillon, J. Fischer, A. A. Jonke, S. Lawroski, W. J. Mecham, W. A. Rodger, W. B. Seefeldt, and V. G. Trice. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

S. LAWROSKI
Director, Chemical Engineering Division
Argonne National Laboratory

contents

contents *(continued)*

REACTOR FUEL PROCESSING

COMMERCIAL ASPECTS OF FUEL PROCESSING

Interim Processing Plans

The Atomic Energy Commission has assigned responsibility to the four locations (Hanford, Idaho, Oak Ridge, and Savannah River) having fuel processing facilities to provide for the processing of spent nuclear fuel elements from privately and publicly owned reactors.[1] The AEC has previously agreed to provide for such processing services until they become available from private sources. Assignments have been made for fuels from 17 specific power and experimental reactors which are already in operation or under construction, as well as from those research and test reactors using uranium-aluminum alloy fuels (see Table I-1). The reactors listed in the assignments include power plants financed in whole or in part by private industry, public or private utilities, or the Federal Government. As other domestic and foreign projects come into operation, they will be assigned in accordance with type and enrichment of fuel involved.

At the AEC-sponsored symposium on Chemical Reprocessing of Power Fuels held Oct. 20 and 21, 1959, at Hanford, the factors were outlined which led to the decision to process returned fuels in the existing facilities at Hanford, Idaho, Oak Ridge, and Savannah River rather than to construct a new multipurpose plant. The possibility that some or all of the irradiated fuels might be accepted by a private processing facility by the middle or late 1960's was a major factor in selecting the alternative with the lowest capital investment. Other factors included the following: (1) capacity of existing plants appeared adequate to handle projected loads for the next several years, (2) technical talent for process development was available at existing sites, and (3) the maximum use of existing fa-

cilities allowed more time for developing new processing techniques and offered more incentive to improve the processes at a later date.[2]

At the same meeting the different dissolution systems to be used were discussed in connection with the fuel types assigned to each site.[3]

Idaho

The Idaho processing systems were installed primarily for process development work. The AEC is making use of these facilities to do the processing work during the interim processing period. Work at Idaho includes sulfuric acid treatment of stainless-steel cermet fuels, hydrofluoric acid treatment of uranium-zirconium alloy fuels, and nitric acid treatment of uranium-aluminum type fuels in a direct-maintained plant of relatively low capacity. Nitric acid dissolution of uranium-aluminum fuels can be done either in a continuous or a batch dissolver system.

Hanford

Hanford plans to use equipment constructed of nickel chrome steel, for example, for sulfuric acid decladding of stainless-steel-clad fuel, for ammonium fluoride decladding of zirconium-clad fuel, and for nitric acid treatment of aluminum-clad fuels. This construction material may be the answer for the long-sought dissolver for these three types of fuel cladding. Provision will be made in the design of the Hanford modification for the later addition of a shear for chopping fuel elements in small fragments. Such a unit would permit greater flexibility and potentially higher capacity in the dissolution equipment.

1

Table I-1   ASSIGNED RESPONSIBILITY FOR PROCESSING[1] POWER AND
EXPERIMENTAL REACTOR FUELS

AEC installation, reactor name, and/or owner	Type of fuel element	Initial uranium enrichment, %
HANFORD		
Dresden Nuclear Power Station, Commonwealth Edison Co.	UO_2 in Zr tubes	1.5
Yankee Atomic Electric Co.	UO_2 in S.S. tubes	2.6
Shippingport Atomic Power Station (blanket only), AEC and Duquesne Light Co.	UO_2 in Zr tubes	Natural
Pathfinder Plant, Northern States Power Co.	UO_2 in Al–Ni plates	1.8
Piqua, AEC and City of Piqua, Ohio	U clad with Al–Ni	1.8
OAK RIDGE NATIONAL LABORATORY		
Enrico Fermi Atomic Power Plant (blanket only), Power Reactor Development Co.	U-Mo alloy in S.S. tubes	Depleted
Hallam Nuclear Power Facility, AEC and Consumers Public Power District	U-Mo alloy in S.S. tubes	3.5
N. S. *Savannah*, AEC and Maritime Administration	UO_2 in S.S. tubes	4.1
Consolidated Edison Thorium Reactor, Consolidated Edison Co. of New York	ThO_2-UO_2 in S.S. tubes	90
Elk River, AEC and Rural Cooperative Power Assn.	ThO_2-UO_2 in S.S. tubes	90
BORAX-IV (Boiling Reactor Experiment No. 4), AEC	ThO_2-UO_2 in tubed Al plates	90
EBWR (Experimental Boiling Water Reactor), AEC	U-Zr alloy in Zr plates	1.5
SRE (Sodium Reactor Experiment), AEC and Southern California Edison Co.	U rods in S.S. tubes	3.5
Research reactors, foreign	U-Al alloy	20
SAVANNAH RIVER		
Enrico Fermi Atomic Power Plant (core only)	U-Mo alloy clad with Zr	27
IDAHO CHEMICAL PROCESSING PLANT		
Shippingport Atomic Power Station (core only)	U-Zr alloy clad with Zr	90
OMRE (Organic Moderated Reactor Experiment)	U-S.S. mixture clad with S.S.	90
SM-1 (Stationary Medium Power Plant),* AEC and U. S. Department of the Army	U-S.S. mixture clad with S.S.	90
VBWR (Vallecitos Boiling Water Reactor), General Electric Co. and Pacific Gas and Electric Co.	U-S.S. mixture clad with S.S.	90
SL-1 (Stationary Low Power Plant No. 1),† AEC	U-Al-Ni in Al-Ni plates	90
Research and test reactors, domestic and foreign	U-Al alloys	90

*Formerly called the APPR.
†Formerly called the ALPR.

Oak Ridge

Oak Ridge facilities, as those at Idaho, have been primarily built for process development work. The AEC is making use of these facilities to process fuels on a routine basis during the interim processing period. The process selected by Oak Ridge can dissolve stainless-steel cladding with sulfuric acid and zirconium cladding with ammonium fluoride in Nionel equipment. An alternate process for dissolving stainless steel to be installed at Oak Ridge, under its development program, is the Darex facility which uses a hydrochloric−nitric acid combination as the dissolving agent to achieve complete dissolution. Also to be included is mechanical decladding equipment for some of the fuels. The Oak Ridge facility is a direct-maintained plant of low capacity. In contrast to only modifying existing facilities, as will be the case at other sites, Oak Ridge will also build a separate head-end treatment unit consisting of two processing cells, an unloading basin, and a storage canal.

Savannah River

Savannah River now plans to use a combination of hydrofluoric acid and nitric acid to dissolve Power Reactor Development Co. (PRDC) zirconium-clad pins and nitric acid to dissolve the Canadian fuels using existing dissolvers of type 309 Cb-stabilized stainless steel. The PRDC core contains stainless-steel bird cages to hold the zirconium pins in a fixed geometry, and Savannah River plans to use a removable basket for accumulating undissolved stainless-steel pieces.

As part of this program, the General Electric Co. has announced that it is beginning detailed design of additional facilities for Hanford's chemical processing plant to enable handling 50 to 150 tons of spent fuel elements per year from power reactors now under construction throughout the nation.[4] Six million dollars' worth of facilities, mostly modifications of those in which Hanford now processes spent fuel elements from production reactors, will accommodate highly diversified fuel material with up to 5 per cent U^{235} enrichment. Completion is scheduled for 1961. The architect-engineer for this design project is Vitro Engineering Corp.[5]

This year's "omnibus bill," as approved by the Joint Committee on Atomic Energy, contains a provision that would allow the AEC to enter contracts with its nuclear material licensees under which the AEC would provide chemical processing services for irradiated reactor fuel.[6] Up to now the AEC could provide such services directly only to licensed reactor operators. The new provision would make it possible for nuclear fuel fabricators to offer to reactor operators a complete "package" fuel-cycle service.

Cost Information

When the AEC established its basic charge of $15,300 per day of plant operation for processing irradiated reactor fuel,[7] it said the charge was based on an assumed plant with a capacity of 1 ton per day for normal or slightly enriched uranium and a reduced capacity for more highly enriched uranium. The basic charge thus equals approximately $17 per kilogram of uranium processed. Last month the AEC said in a report on "Costs of Nuclear Power" that the AEC charge per kilogram of contained uranium varies with type of reactor fuel[6] (see Table I-2).

Table I-2   AEC PROCESSING CHARGES* FOR VARIOUS REACTOR FUELS[6]

Reactor	Fuel-element type	Processing site	AEC charge, $/kg U
Dresden	UO_2, Zr clad, 1.5% U^{235}	Hanford	24
Yankee	UO_2, S.S. clad, 2.6% U^{235}	Hanford	21
Hallam	U–Mo, S.S. clad, 2.5% U^{235}	Hanford	20
PRDC (blanket)	U–Mo, Zr (S.S.?) clad, depleted U	Hanford	19
PRDC (core)	U–Mo, Zr clad, 27% U^{235}	Savannah River	139
Indian Point	UO_2–ThO_2, S.S. clad, 90% U^{235}	Oak Ridge	1240

*The basic charge of $15,300 has since been increased to $16,260 to reflect increases in construction costs over original capital investment estimates. Thus the figures in the last column should be increased proportionately.

In 1957 when the AEC fixed the price schedule for the buy-back of plutonium produced in licensed power and research reactors in the United States, it said that up to July 1, 1962, the price would range between $30 and $45 per gram of plutonium metal, depending on the Pu^{240} content (an undesirable contaminant). Recently the AEC spelled out this schedule in more detail.[6] The $45 per gram price holds only where

no Pu^{240} is present. Where the Pu^{240} content is 8.6 per cent and above, the $30 per gram price applies. Between these two points, the AEC has established the following per gram price steps: 2 per cent Pu^{240}, $41.50; 4 per cent Pu^{240}, $38.00; 6 per cent Pu^{240}, $34.50; 8 per cent Pu^{240}, $31.00.

Uranium Procurement and Production Statistics

The AEC has made public its statistics[8] on uranium-concentrate (U_3O_8) procurement from domestic and foreign sources for the 12 fiscal years 1948 to 1959. Also included is a combined total of U. S. concentrate procurement from 1943 to 1947, which includes purchases made by the Manhattan Engineer District during and directly following World War II. These data are shown in Table I-3.

Table I-3   URANIUM-CONCENTRATE PROCUREMENT[8] FOR FISCAL YEARS 1943 THROUGH 1959

Fiscal years	Tons of U_3O_8		
	Domestic	Foreign	Total
1943–1947	1,440	10,150	11,590
1948	110	1,960	2,070
1949	120	1,960	2,080
1950	320	2,740	3,060
1951	630	3,050	3,680
1952	830	2,830	3,660
1953	990	1,910	2,900
1954	1,450	3,240	4,690
1955	2,140	3,800	5,940
1956	4,200	6,240	10,440
1957	7,580	8,580	16,160
1958	10,250	16,130	26,380
1959	15,160	18,170	33,330

The AEC has also announced monthly and total statistics[9] on domestic uranium production for the first six months of calendar year 1959. Included are figures on uranium concentrates, domestic ore production, rate of processing, ore fed to process, ore stockpiling, ore reserves, and initial production bonus payments.

Domestic ore reserves were estimated to total 88,900,000 tons on July 1, 1959. In addition, ore stockpiles totaled 1,451,625 dry tons. Ore receipts at all private plants and Government purchase depots for January to June 1959 totaled 3,310,000 dry short tons; ore fed to process totaled 3,614,000 tons, with an average grade of 0.25 per cent U_3O_8. Uranium concentrates received at the Grand Junction depot totaled 8298 tons of U_3O_8 in the six-month period.

As of June 30, 1959, there were 23 uranium processing mills in operation, including the single Government-owned mill at Monticello, Utah. Their combined rated daily capacity was approximately 21,740 tons of ore per day; their total estimated capital investment was about $138,550,000. Two additional mills with total rated capacity of 1014 tons of ore per day were under construction in Fremont and Natrona Counties, Wyoming.

Waste-disposal Licensing

The license request of a Houston, Texas, firm[10, 11] to dispose of wastes into the Gulf of Mexico has run into further trouble.[12] On Sept. 3, 1959, the Commission issued an order granting the State of Texas, through its Attorney General, permission to intervene in the proceeding. On Sept. 25, 1959, the AEC, as a result of views expressed to the Commission by the Department of State concerning disagreement by the Government of Mexico to the issuance of the proposed license, determined that the public interest requires postponement of scheduled oral argument for at least 60 days during consideration of this disagreement and ordered the matter set down for oral argument before the Commission on Dec. 17, 1959.

The AEC has announced intention to issue licenses to two California companies (Ocean Transport Company of San Franciso and California Salvage Company of San Pedro) to dispose of low-level waste into the Pacific Ocean at depths greater than 1000 fathoms.[13, 14]

Scrap Recovery Contracts

The AEC New York Operations Office has announced the award of (1) a $77,100 contract to Nuclear Materials & Equipment Corp. to recover approximately 29 kg of uranium from (a) uranium-zirconium-alloy saw and milling chips, (b) solutions containing sulfates, nitrates, and fluorides, and (c) miscellaneous samples; and (2) a $6047 contract to Engelhard Industries, Inc., to recover approximately 7.5 kg of uranium from (a) uranium-aluminum alloy in the form of chips and solid pieces of alloy and (b) skulls and

dross and laboratory solutions containing borates, fluorides, and nitrates.[4]

Radioactive Shipments

The AEC has drafted specific criteria to be used by the Idaho Chemical Processing Plant, Oak Ridge National Laboratory, Hanford Works, and Savannah River Plant in accepting for chemical processing irradiated reactor fuels from commercial power plants.[4] Among the items covered in the four separate general cask-acceptance criteria are: (1) acceptable methods of transportation and corresponding destination points; (2) acceptable radiation, contamination, pressure, and temperature levels; (3) physical limitations on cask design in length, width, height, and weight; (4) details concerning transfer of the shipping cask from the transportation vehicle to the installation's storage facility; (5) details on fuel-element packing and criticality; and (6) other general considerations.

The AEC also said that its Division of Licensing and Regulation is currently formulating a proposed regulation (to be published in the near future) covering the issuance of licenses for the transfer of irradiated solid reactor fuels. The draft regulation will state criteria for use in container design and shipping procedures and is understood to cover the following points with respect to the shipping cask: criticality, heat removal, radiation levels outside the cask, contamination levels, and structural integrity.

An international panel of experts on transportation of large radioactive sources and fissionable material, including spent fuel elements, has been set up by the International Atomic Energy Agency to begin the drafting of regulations "providing minimum safety measures as universally acceptable and as uniform as possible for air, water, and land transportation." The chairman of the panel is H. N. Sethna, head of the Chemical Engineering Division of the Indian Atomic Energy Establishment; the U. S. representative is Lester R. Rogers of the AEC.[4]

References

1. AEC Announces Assignments for Fuel Reprocessing, AEC Press Release IN-27, Oct. 15, 1959.
2. G. F. Quinn, Objectives of the AEC Power Fuel Processing Program, Talk Presented at Interim Reprocessing Program Meeting, Hanford, Washington, Oct. 20–21, 1959.
3. F. P. Baranowski, Scope of Power Fuel Processing Program, Talk Presented at Interim Reprocessing Program Meeting, Hanford, Washington, Oct. 20–21, 1959.
4. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., Vol. 6, No. 8, August 1959.
5. *Chemical Engineering*, 66(17): 53 (Aug. 24, 1959).
6. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., Vol. 6, No. 9, September 1959.
7. *Reactor Fuel Processing*, 1(1): (February 1958).
8. U. S. Uranium Concentrate Procurement Statistics for 1948-1959 Made Public by AEC, AEC Press Release B-166, Sept. 23, 1959.
9. Domestic Uranium Production Statistics for First Half of 1959 Announced by AEC, AEC Press Release B-166, Sept. 9, 1959.
10. *Reactor Fuel Processing*, 2(4): (October 1959).
11. *Reactor Fuel Processing*, 2(3): (July 1959).
12. Highlights of AEC Licensing Activities for August–September 1959, AEC Press Release IN-26, Oct. 8, 1959.
13. AEC Proposes to Issue Waste Disposal License to Ocean Transport Company, AEC Press Release B-160, Sept. 15, 1959.
14. AEC Proposes to License California Firm to Dispose of Low-level Wastes in Pacific, AEC Press Release B-157, Sept. 9, 1959.

Chemical and mechanical methods are being developed for decladding, dissolution, and head-end treatment for a wide variety of fuels. Decladding may be accomplished mechanically or chemically; dissolution is performed chemically, the exact treatment depending on the composition of the fuel.

Mechanical Processing

Many nuclear reactor fuels now being used are clad with materials that will not dissolve in nitric acid. The removal of the cladding by mechanical means will make possible a conventional nitric acid dissolution of the fuel. Also, mechanical removal of the cladding means smaller aqueous waste volumes and increased plant capacity in the absence of dissolved cladding material being added to process streams.

Several methods of mechanical processing are being examined at Hanford Atomic Products Operation (HAPO).[1-5] These include sawing and shearing. In cold-sawing studies,[3,4] initial operation of a milling-cutter "coldsaw," being tested for power fuels end-fitting cutoff, showed that the blades may be expected to process at least 50 tons of fuel if proper work clamping can be employed. About 2700 sq in. of stainless steel has been cut without detectable dulling of the blade, saw horsepower increase, or gross change in chip appearance. The resultant chips (about $\frac{3}{32}$ by $\frac{3}{8}$ in.) have a bulk density of 75 to 100 lb/cu ft. With the blade-life test completed, future studies will include: (1) water-lubricated sawing (without cutting-oil additive), (2) extra-thin wall tubing cuts, (3) simulated Dresden type hardware cuts, and (4) cuts on rod bundles with interiors inaccessible for shimming.

Underwater shearing studies have been conducted[5] using stainless-steel-clad swaged uranium dioxide fuels to determine the characteristics of the uranium dioxide — water suspension formed during shearing. Semiquantitative measurements indicate that as much as 3 per cent of the uranium may be suspended during normal shear operation. Microscopic examination indicated that the suspended particles are mainly in the 10- to 20-μ range, although settling rates (0.04 mm/sec) indicate the presence of some 3- to 5-μ particles.

Tests of a combination consisting of a stainless-steel male V moving blade and a semicircular stationary blade[3,5] show that this combination cuts with lower forces than any other tried to date and that rod bundles disintegrate more thoroughly. The 40-ton shear,[1] using a tool-steel moving blade and a stainless-steel stationary blade, has completed several thousand cuts, totaling 10,000 sq in. cross-sectional area of cut material. This service is equivalent to the shearing of approximately 2 tons of power reactor fuel elements. When extrapolated to production shears, the blade deterioration data indicate that shear cutting-force requirements will be increased at the rate of 1 ton for each ton of uranium chopped. For example, if a 150-ton force is initially required for a new blade, a force of 170 tons would be required for the same fuel when the blade had chopped 20 tons.

The shearing tests on stainless-steel-clad, porcelain-filled prototype fuel with eight different blades in combination with three different anvils were completed both at Oak Ridge National Laboratory (ORNL)[6,7] and under two subcontracts. The conclusions from these tests were: (1) optimum initial clearance between blades is 1 to 3 mils; (2) rounding of the cutting edge of the shear blade to a 0.03- to 0.05-in. radius does not impair cutting efficiency and minimizes chipping of the cutting edge; (3) the combination of a stepped cutting blade and a concave anvil produces the best cuts and breakout of ferrules for minimum tonnage; and (4) a blade hardness between Rockwell C54 and C56 appears optimum. Hardness above C56 results in cracking of the blades, and hardness below C54 results in excessive wear, galling between blades, and breakage of the cutting edges when shearing through brazing alloy, which has a Rockwell hardness of C51.

In connection with shearing-leaching tests,[8-10] the percentage (P) of powdered (median size 250 μ) uranium dioxide produced in shearing 0.4-in.-diameter uranium dioxide-filled stainless-steel tubes was related to the length of cut (L) by $P = 13/L^{1.2}$ for 0.5- to 5-in. lengths. It was also demonstrated that stainless-steel particles up to 1000 μ in diameter can be satisfactorily jetted from a batch dissolver.

In tests at ORNL,[11] abrasion-disk sawing of end boxes from Consolidated Edison prototype elements was done at rates up to 60 in./min, although 25 to 30 in./min was optimum. At this rate about 7 g of metal is produced per gram of abrasive consumed. Only friction sawing appeared to be adequate for simultaneously sawing metal and uranium oxide.

The Sodium Reactor Experiment (SRE) fuel decladding equipment was received and was installed for preliminary testing.[8] This equipment, which removes the inert-end hardware and expels the fuel pins, was operated with only minor malfunctions.[12]

Laboratory tests showed[7-10,13] that steam at rates up to 0.4 lb/hr (per 98 ml of NaK) and possibly higher would be a satisfactory reagent in reacting the NaK thermal bonding agent for disposal as waste. The reaction proceeded uneventfully at a hydrogen evolution of ~1 liter/min for a 35-min period while reacting 98.4 ml of NaK, the total volume contained in a single SRE element. A reaction temperature of 290 to 320°C was measured. A device for handling deformed SRE fuel tubes, for which the standard SRE decladder is not adapted, was designed, fabricated, and successfully tested. This machine requires that the fuel tube first be cut into 6-in. lengths.

Chemical Dejacketing

An attractive alternate to mechanical dejacketing or complete dissolution is selective chemical dissolution of fuel jackets and structural components. This permits the exposed fuel core to be dissolved in another (probably less corrosive) reagent in a second step. Aluminum, stainless steel, and zirconium or Zircaloy are the principal jacket materials now in use. A new proposal is nickel coatings for aluminum jackets.

Removal of Zirconium and Zircaloy Jackets

The Zirflex process in which $6M$ ammonium fluoride–$1M$ ammonium nitrate is used as a dissolving agent for zirconium- or Zircaloy-clad fuel elements having either an oxide core or a uranium-niobium-zirconium alloy core continues to be studied at HAPO[1-5,14] and ORNL (references 6, 11, 15, and 16).

A point of some concern in the Zirflex process is the fact that U(VI) is relatively soluble in the terminal solution resulting from a Zirflex decladding operation. In particular, any uranyl nitrate solution left as a heel in a dissolver might be lost to the cladding waste in a subsequent Zirflex decladding step. Fortunately, however, laboratory studies at HAPO[4] in both glass and stainless-steel equipment indicate that dissolution of Zircaloy-2 by either ammonium fluoride or ammonium fluoride–ammonium nitrate solutions containing U(VI) results in rapid and nearly complete reduction of uranium to the less soluble U(IV) for all conditions of practical interest.

Additional Zirflex dissolution runs have been carried out[3,5] to confirm earlier data on ionic conductance as an index of completeness of zirconium dissolution. On the basis of these and previous data, the ionic conductance can serve as an empirical index of the completeness of zirconium dissolution in the Zirflex process.

Fifteen Pressurized Water Reactor (PWR) blanket fuel specimens (normal uranium dioxide pellets encased in Zircaloy-2) varying in burn-up from 80 to 1100 Mwd/ton were declad with boiling $6M$ ammonium fluoride–$1.0M$ ammonium nitrate, after which the uranium dioxide core was dissolved in $10M$ nitric acid.[16] Uranium and plutonium losses to the decladding solution were less than 0.2 per cent in nearly all runs. In two runs where $9M$ hydrofluoric acid was used as the decladding reagent, the uranium and plutonium losses averaged 1.0 and 0.4 per cent, respectively. Other studies at the Idaho Chemical Processing Plant (ICPP)[17,18] and the Savannah River Plant (SRP)[19,20] have shown that zirconium cladding can be removed in more dilute hydrofluoric acid with low uranium losses.

In studies at Chalk River[21] the removal of zirconium cladding by scoring the sheath through to the uranium and contacting the assembly with steam at 340 to 380°C was demonstrated. The steam converts the uranium to a mixture of

uranium dioxide and U_3O_8, and the expansion accompanying formation of this material causes the sheath to peel away from the fuel. The resulting mixture of uranium oxides is dissolved in nitric acid, leaving the zirconium behind.

Zirconium removal by high-temperature oxidation (800 to 1000°C) was also successful,[21] and the chief problem was selection of proper container materials. In the process zirconium is converted to zirconium dioxide, and uranium is converted to uranium dioxide. After cooling is completed, the uranium dioxide is leached away from the insoluble zirconium dioxide with nitric acid.

Removal of Stainless-steel Jackets

Sulfex flow sheets for Yankee Atomic Power Reactor fuel have been presented in an earlier Review.[22] In recent studies[11] the passivation of stainless steel that occurred when stainless-steel-clad uranium dioxide (Yankee type fuel) was declad with $6M$ sulfuric acid was found to be caused exclusively by nitric acid carried over from prior uranium dioxide core dissolutions. Passivation was produced by as little as $10^{-4}M$ nitric acid in $6M$ sulfuric acid. Addition of formic acid to destroy the nitric acid resulted in rapid initiation of the sulfuric acid – stainless-steel reaction. Decladding was achieved in 1.75 to 2 hr. Uranium losses observed in decladding of stainless-steel-clad uranium dioxide fuels increase with the degree of fuel-pellet fragmentation and exposure time to the sulfuric acid. Uranium and plutonium losses in a 2-hr decladding of a Yankee Atomic fuel pin irradiated to 1440 Mwd/ton were 0.045 and 0.052 per cent, respectively. However, uranium and plutonium losses were as high as 20 per cent when irradiated core material was exposed to boiling fresh decladding solution, in the presence of oxygen, for 24 hr. Irradiated uranium dioxide dissolved much more rapidly in nitric acid than did unirradiated uranium dioxide.

In studies of the Sulfex process at HAPO,[1-5] the effect of nitrate ion on the dissolution of 304-L stainless steel and of uranium dioxide in sulfuric acid was examined to determine the required cleanout of the dissolver from batch to batch. It appeared desirable to keep nitrate concentration to $0.01M$ or less during Sulfex decladding.

Passive films on stainless steel in contact with platinum were not depassivated after several hours in boiling $6M$ sulfuric acid. In decladding tests[7] on an irradiated (~ 1000 Mwd/ton) Yankee Atomic fuel pin (in a platinum basket), formic acid did not break passivation in 1 hr. However, the pin was depassivated in less than 5 min in $12M$ sulfuric acid; the dissolvent was then diluted to $6M$ sulfuric acid, and decladding was completed in 1.25 hr. Uranium and plutonium losses after a total reaction time of 2 hr were 0.07 and 0.18 per cent, respectively. These tests will be repeated in a Nionel basket using boiling $0.1M$ formic acid – $6M$ sulfuric acid to determine whether passivation of irradiated samples can be broken by formic acid in the absence of platinum.

In the decladding of Consolidated Edison (stainless-steel-clad thorium dioxide – 4 per cent uranium dioxide) fuel with $6M$ sulfuric acid (references 7, 11 – 13, and 15), uranium losses were highly dependent on the amount of U_3O_8 in the uranium dioxide; losses from air-fired (predominantly U_3O_8) and hydrogen-fired uranium dioxide varied by factors of 10 to 30. With 200 per cent excess sulfuric acid, the uranium losses for 6 hr decladding of unirradiated thorium dioxide – U_3O_8 Consolidated Edison fuel pins were 0.1 to 0.2 per cent versus <0.02 per cent for thorium dioxide – uranium dioxide pellets. The maximum uranium and thorium losses during a 3-hr exposure of finely pulverized thorium dioxide – uranium dioxide irradiated to 5600 Mwd/ton and decayed for 4 years were 3 and 0.3 per cent, respectively.

In engineering-scale tests[12,15] on semicontinuous decladding of Consolidated Edison fuel, 15.5-kg samples of type 304 stainless steel were dissolved continuously in boiling $6M$ sulfuric acid at a rate directly proportional to the dissolvent flow rate. The product concentration was maximum, 62 g of stainless steel per liter, at $4.7M$ sulfuric acid; at this point the dissolution rate was $1.6 \text{ mg/(cm}^2)(\text{min})$. The mole ratio of nitrogen generated to stainless steel dissolved was 1.13. These data indicate a decladding time of 4 hr for a Consolidated Edison element, assuming uniform attack.

A small engineering-scale trial Sulfex run was successfully made[6] in which nearly all of a dummy 11-plate stainless-steel fuel assembly weighing 7.75 kg was dissolved in boiling $6M$ sulfuric acid at an approximate rate of 83 g of stainless steel per minute. Hydrogen was evolved into the nitrogen gas blanketing the system at about 1.28 cu ft/min (S.T.P.).

In the first series of pilot-plant runs at HAPO[4] involving the dissolution of 304-L stainless steel by the Sulfex process, the quantity of hydrogen observed in the off-gas was somewhat lower than the stoichiometric quantities. The relative quantities of hydrogen in the off-gas very closely followed the course of the reaction and were used to determine the start and the end of the dissolution. In use of decladding solutions containing $2.9M$ to $4.1M$ sulfuric acid, no precipitation was experienced up to $1.1M$ stainless-steel concentration. With concentrations of $1.3M$ stainless steel, a heavy precipitate occurred when the decladding solution was cooled to room temperature.

The Darex process dissolvent (mixed nitric and hydrochloric acids) was used to declad stainless-steel-clad uranium dioxide – thorium dioxide fuels in experiments at ORNL with non-irradiated fuel.[11] Chloride holdup by the declad oxide pellets was sufficiently low after water washing to produce uranium-thorium feed solutions containing <300 ppm chloride. Twenty-five unirradiated simulated Consolidated Edison fuel pins were declad and dissolved in succession[6] in a titanium dissolver. Uranium losses to the $5M$ nitric acid – $2M$ hydrochloric acid decladding solution varied in a random manner from 0.1 to 0.5 per cent over the 25 cycles. Dissolution of the 95.5 per cent thorium dioxide – U_3O_8 core pellets (~80 per cent of theoretical density) in $13M$ nitric acid – $0.04M$ sodium fluoride – $0.1M$ aluminum nitrate was complete at the end of each cycle.

Dissolution of stainless steel by anodic oxidation is a possible method for dejacketing stainless-steel-clad fuel elements. Laboratory investigations at SRP[23] showed that the dissolving rates of stainless steel in nitric acid by this method depend only on current density and that the containing vessel would undergo only moderate corrosion, about 10 mils/year. Dissolving rates obtained with direct current were about 0.6 g/(amp)(hr), corresponding to penetration rates of 30 mils/hr at a current density of 1 amp/cm^2.

Removal of Aluminum Jackets

Aluminum can be dissolved away from uranium metal, uranium oxide, thorium metal, and thorium oxide in caustic soda according to the basic equation

$$Al + NaOH + H_2O \rightarrow NaAlO_2 + 1.5H_2$$

At Chalk River[21] the hydrogen explosion hazard has been eliminated by diluting the off-gases with air to below the explosive limit of 4 per cent. At some U. S. projects air is allowed to leak into the dissolver to eliminate the hydrogen explosion hazard; at other U. S. projects sodium nitrate is added to the solution[29] to convert the hydrogen to ammonia. For BORAX-IV fuel the presently preferred method for processing (references 7, 9–11, and 13) is removal of the aluminum cladding with boiling $2M$ sodium hydroxide – $1.78M$ sodium nitrate, dissolution of the lead bond in $1M$ to $2M$ nitric acid, and dissolution of the sintered thorium dioxide – U_3O_8 core in boiling $13M$ nitric acid – $0.04M$ sodium fluoride – $0.1M$ aluminum nitrate. The initial rate of dissolution of lead foil increased from 3.3 to 15.9 mg/(min)(cm^2) as the nitric acid concentration was increased from $0.5M$ to $2.0M$. Decladding with mercury-catalyzed nitric acid was unsatisfactory because a mercury concentration of $0.5M$ is required to assure an adequate dissolution rate. This is about 10 times the concentration normally required for dissolution of aluminum.

Several procedures for dissolving the nickel coating, proposed for aluminum-clad production elements to increase corrosion resistance, are being tested at HAPO.[1,3] Boiling nitric acid dissolved the coating at penetration rates which increased exponentially from about 0.05 mil/hr at $0.05M$ nitric acid to about 35 mils/hr at $3M$ nitric acid. Off-gas from dissolution of nickel cladding in $3M$ nitric acid is principally oxides of nitrogen with only traces (0.1 to 0.3 vol.%) of hydrogen. Penetration rates in boiling $1.5M$ uranyl nitrate hexahydrate – nitric acid solutions were factors of 10 to 20 higher than in nitric acid alone. Removal of nickel cladding with uranyl nitrate hexahydrate – nitric acid dissolver solutions would be feasible, therefore, if introducing small amounts of nickel into the Purex process is not considered objectionable.

Dissolution

Simultaneous Dissolution of Jacket and Core

1. *Zirconium Fuel Elements*. Several promising methods have been proposed for simultaneous dissolving jacket and core of fuel elements containing zirconium. These include

hydrochlorination (Zircex process), aqueous fluoride—nitric acid mixtures, and hydrofluoric acid—hydrogen peroxide (Perflex process).

In the Zircex hydrochlorination process, zirconium-clad uranium-zirconium and uranium-zirconium-niobium fuels are hydrochlorinated at ~500°C to produce volatile zirconium chloride and nonvolatile uranium trichloride, thereby separating uranium and zirconium.[11] For high zirconium-uranium alloy fuels, a small portion of the uranium formed a zirconium dioxide—uranium dioxide solid solution during hydrochlorination, which resulted in ~1.5 per cent insoluble uranium loss during nitric acid leaching of the uranium trichloride. When the residue was contacted with gaseous carbon tetrachloride—nitrogen at 600°C, uranium tetrachloride and zirconium chloride were formed, which, when desublimed, were totally soluble in nitric acid. The resulting fuel solution contained 10 moles of zirconium per mole of uranium but only 2 per cent of the zirconium originally present in the fuel.

Separation of uranium chlorides from zirconium chloride by fractional desublimation at 300°C was demonstrated.[6] A mixture of carbon tetrachloride—hydrochloric acid was used to remove all uranium as tetrachloride from the hydrochlorination residue in the reactor to the 300°C glass-wool-packed desublimer.

Recent Zircex experiments on PWR blanket fuel rods[21] (zirconium-clad uranium dioxide) completely removed zirconium with a total uranium loss of only ~0.01 per cent. Absorption of chlorine by the unreacted uranium dioxide pellets was approximately 1 per cent. Reaction temperatures in these runs had been increased to 600 to 700°C. No data are available on uranium losses in hydrochlorinating zirconium-clad uranium-metal or thorium-metal fuels.

In the Perflex process,[10] uranium-zirconium alloy fuels are dissolved in aqueous hydrofluoric acid—hydrogen peroxide. A 7 per cent uranium—93 per cent zirconium alloy was readily dissolved in this reagent. In corrosion studies[11, 12, 15] with Monel and INOR-8, neither was sufficiently corrosion-resistant for use as a process vessel.

Studies of the dissolution kinetics of zirconium in hydrofluoric acid—nitric acid are being made (references 4, 17, 18, and 24). The activation energy for the initial rate of dissolution of zirconium in $0.5M$ hydrofluoric acid—$13M$ nitric acid was calculated to be 5.8 kcal/mole at temperatures below reflux. For hydrofluoric acid concentrations ranging from $0.5M$ to $2.0M$, dissolution rates were high (2 to 9 $g/(cm^2)(hr)$) and essentially unaffected by nitric acid in concentrations[4] from $0M$ to $5M$.

2. *Stainless-steel Fuel Elements*. Fuel elements containing stainless steel may be dissolved in dilute aqua regia (Darex), in dilute sulfuric acid (Sulfex), and in nitric acid—ammonium bifluoride mixtures (Niflex).

The three-step Darex process involves dissolution in dilute nitric—hydrochloric acid, chloride removal, and feed adjustment for solvent extraction. In small engineering-scale tests (references 9, 10, 12, and 15) the ORNL reference flow sheet[25] as applied to Yankee Atomic fuel was found to be applicable also to N.S. *Savannah* prototype fuel without modifications and to total dissolution of stainless-steel-clad 5 to 8 per cent uranium dioxide—thorium dioxide (Consolidated Edison fuel) by adding fluoride catalyst to dissolve the mixed oxide pellets. A preliminary Darex flow sheet for Yankee Atomic fuel elements was also presented by Shefcik and Platt[26] at HAPO.

Dissolution of stainless-steel-clad, metallic uranium core fuel elements was continued.[1] The dissolution rate of uranium varied inversely with the nitrate-to-chloride ratio in acid concentrations greater than $2M$. Rates increased from 18 to 169 mils/hr as the nitrate-to-chloride mole ratio decreased from 6.0 to 3.0.

The dissolution of type 304 stainless steel in Darex—uranyl nitrate hexahydrate solutions was studied.[1, 5] The stainless steel would not dissolve in a $1.2M$ uranyl nitrate hexahydrate—$3.3M$ total acid solution in which the nitrate-to-chloride mole ratio was 4.2. Stainless steel dissolved readily at about 30 mils/hr after an initial contact with an activator when the hydrochloric acid was increased to a nitrate-to-chloride mole ratio of 2.9. Previously reported data for the dissolution of stainless steel in the absence of uranyl nitrate hexahydrate show a maximum tolerable nitrate-to-chloride ratio of about 8 for dissolution of stainless steel.

The chloride ion concentration of Darex process dissolver solutions can be reduced readily to 0.1 g/liter or less by simple batch boildown

with the addition of nitric acid.[27] Efficiency of chloride removal is improved by preliminary concentration of the Darex solution; twofold concentration appears optimum. The chloride concentration of a synthetic Darex solution was reduced from 68 to 0.001 g/liter by twofold concentration and subsequent 5-hr batch boildown with the addition of 12.7M nitric acid. The rate of chloride removal varied directly with nitric acid concentration in an Army Package Power Reactor (APPR) type Darex dissolver product containing 100 g/liter metal loading, 0.58M initial chloride, and initial nitric acid concentrations of 8M to 14M (see Table II-1).[28] The removal rate with 8M and 9M nitric acid was very low.

An electrolytic method of dissolving stainless-steel-containing fuel elements is being developed at ICPP.[17,18,28] During the electrolytic dissolution of stainless steel – UO_2 fuels in nitric acid, the uranium dioxide dissolves in a simple chemical reaction with the acid. A review of dissolver operating conditions has shown that temperatures of 100°C or higher and acid concentrations of 0.6M or more are needed to ensure complete uranium dioxide dissolution in $\frac{1}{2}$ hr.

Dissolution of Dejacketed Material

Dissolution of the core is possible if fuel jackets can be removed mechanically or physi-

Table II-1   CHLORIDE REMOVAL FROM APPR DAREX DISSOLVER PRODUCT* AS A FUNCTION OF REFLUX TIME AND NITRIC ACID CONCENTRATIONS

Reflux time, hr	8M initial HNO_3 Cl content, M		9M initial HNO_3 Cl content, M		10M initial HNO_3 Cl content, M		12M initial HNO_3 Cl content, M		14M initial HNO_3 Cl content, M	
	Sparge	No sparge	Sparge	No sparge	Sparge	No sparge	Sparge	No sparge	Sparge	No sparge
1	0.15	0.57	0.062	0.50	0.0215	0.31	0.0013	0.14	0.0008	0.022
2	0.08	0.54	0.03	0.42	0.0093	0.20	0.0007	0.04	0.00035	0.012
3	0.062	0.54	0.0176	0.38	0.0047	0.15	0.00051	0.0146	< 0.00028	0.0037
4	0.048	0.54	0.0124	0.34	0.0024	0.11	0.00037	0.006	< 0.00014	0.0018
5	0.0415	0.53	0.0095	0.31	0.0018	0.092	0.00034	0.004	< 0.00014	0.0012
6	0.034	0.50	0.0072	0.30	0.0013	0.064	0.00028	0.0025	< 0.00014	0.0007

*Dissolver product: 100 g APPR metal per liter, 0.58M initial Cl^-, and 8M to 14M initial HNO_3. Condenser: updraft with total reflux. Boilup rate/liquid volume = 1/150 min^{-1}. Air sparge rate/liquid volume = 8.5/1 hr^{-1}

The applicability of the Darex process for the dissolution of uranium-molybdenum alloys was reexamined [1,3,5] since a better understanding of the role of ferric ion in preventing molybdenum precipitation now exists. By using uranium – 3 wt.% molybdenum alloy, solutions stable to precipitation following chloride removal have been prepared. A mole ratio of stainless steel to uranium of approximately 1.2 was used. Small amounts of solids were formed during the dissolution. During chloride removal larger amounts of solids were formed. These redissolved in the final concentration step following chloride removal, and a solid-free solution was obtained by diluting to volume at about 0.7M acid. No conditions for preparing solid-free terminal solutions using uranium – 9 wt.% molybdenum alloy have been found as yet. Chloride removal in the presence of molybdenum appeared to proceed about the same as in its absence.

cally, or it may be performed when the fuel is sheared into pieces. Then a more simple dissolution procedure may be possible than when combined jacket-core dissolution is carried out.

The nitric acid – ferric nitrate solutions proposed for dissolution of uranium-molybdenum alloy fuel cores are relatively corrosive, particularly at high concentrations.[1,5] A survey of dissolving rates and solution stability at ferric nitrate concentrations of less than 1M is being made to assist in choosing a dissolving schedule which will minimize corrosion. As expected, lower terminal uranium and higher terminal acidities are required to maintain solution stability. Stability of solutions stored at room temperature is very good; some solid formation has occurred in those stored at 50°C. Addition of dichromate to the solutions appeared to enhance their stability and also served to oxidize plutonium to the hexavalent state during storage.

For dissolution of Consolidated Edison 96 per cent thorium dioxide – 4 per cent uranium dioxide sintered pellets, the use of the Thorex dissolvent containing $13M$ nitric acid, $0.04M$ sodium fluoride, $0.1M$ aluminum nitrate is under study. The presence of boric acid, a possible addition for criticality control, did not affect the dissolution time of ThO_2-UO_2 pellets in Thorex dissolvent.[9,10] The solubility of boric acid in the dissolvent increased from $0.26M$ at $23°C$ to $1.18M$ at $85°C$. The use of sulfuric acid decladding results in the formation of a relatively insoluble layer of thorium sulfate on the fuel pellets. This coating decreased pellet dissolution rates in Thorex dissolvent, and the presence of $0.1M$ sulfuric acid in this dissolvent decreased the dissolution rate by a factor of 8. Addition of ferric nitrate to the dissolvent in concentrations up to $0.5M$ increased the dissolution of high-density unirradiated pellets in 200 per cent excess boiling $13M$ nitric acid – $0.04M$ sodium fluoride to a maximum of 90 per cent in 5 hr. The amount of pellets dissolved in 1 hr in the reagent plus $0.5M$ ferric nitrate plus sulfate ion decreased from 40 per cent to 2 per cent as the sulfate was increased from $0M$ to $0.3M$. Studies are being made of recovery of uranium and thorium from graphite fuels. Process flowsheet development for uranium carbide – graphite fuel compacts indicated[11] that the uranium can be recovered quantitatively (99.8 per cent) by grinding the compact to 200 mesh and leaching with boiling $15.8M$ nitric acid. By a grind leach process, >99.9 per cent of the uranium was recovered from 5.5, 9.7, and 14.0 wt.% uranium (as carbide) in graphite specimens.[9,10] The samples were ground to −200 mesh and leached twice for 4 hr with boiling $15.8M$ nitric acid, and the residue was washed thoroughly with cold water. Three spherical Pebble Bed Reactor fuel samples which had been ground to −200 mesh were leached[12,15] in the same manner. Uranium recovery was 99.9 per cent from the two ungraphitized admixture specimens but only 98.1 per cent from the solution-impregnated ball. Leaching of high density, admixture, graphitized, 4 per cent uranium-graphite fuel with two portions of boiling $15.8M$ nitric acid resulted in a 99.6 per cent recovery of the uranium from −16 +30 mesh samples.[6,7]

Grinding and leaching of thorium carbide – uranium carbide – graphite fuel compacts either in $15.8M$ nitric acid or in $13M$ nitric acid – $0.04M$ sodium fluoride – $0.1M$ aluminum nitrate resulted consistently in ~10 per cent uranium and thorium insoluble losses; however, burning in air or oxygen permitted recovery of >99.9 per cent of both uranium and thorium when the ash was dissolved in the latter dissolvent. Soxhlet extraction of plates of the General Atomics 1.5 per cent uranium – 7.1 per cent thorium-graphite fuel with azeotropic nitric acid offered no advantages over a single leach with boiling $15.8M$ nitric acid in which 10 per cent of the uranium and thorium were insoluble.

Fuel specimens containing 9 per cent uranium in graphite disintegrated when immersed in liquid bromine at $25°C$ for 3 to 5 hr, but specimens containing 0.7 per cent uranium did not disintegrate after 23 hr.[6,7] A specimen of the General Atomics fuel did not disintegrate. Leaching the powder produced by soaking the 9 per cent uranium-graphite fuel in bromine with two portions of boiling $15.8M$ nitric acid resulted in about 99.8 per cent recovery of the uranium; the same recovery was obtained by mechanically grinding to −4 +8 mesh. However, the uranium recoveries from bromine-treated 0.7 per cent uranium, 2 per cent uranium, and 1.5 per cent uranium – 7.2 per cent thorium fuels, which were then leached with two portions of boiling $15.8M$ nitric acid, were 96, 99, and 94 per cent, respectively. Mechanical grinding of these fuels to −4 +8 mesh and leaching by the same technique resulted in recoveries of only 80, 90, and 89 per cent, respectively.

References

1. L. P. Bupp, Hanford Atomic Products Operation, July 10, 1959. (Unpublished.)
2. V. R. Cooper, Quarterly Report, Technology of Non-Production Reactor Fuels Reprocessing, HW-60928, July 2, 1959. (Unclassified AEC report.)
3. L. P. Bupp, Hanford Atomic Products Operation, Aug. 10, 1959. (Unpublished.)
4. L. P. Bupp, Hanford Atomic Products Operation, Sept. 10, 1959. (Unpublished.)
5. V. R. Cooper, Quarterly Report, Technology of Non-Production Reactor Fuels Reprocessing, HW-62063, Sept. 24, 1959. (Unclassified AEC report.)
6. H. E. Goeller and W. H. Lewis, Oak Ridge National Laboratory, August 1959. (Unpublished.)
7. Oak Ridge National Laboratory, Aug. 6, 1959. (Unpublished.)
8. Oak Ridge National Laboratory, Sept. 4, 1959. (Unpublished.)
9. H. E. Goeller and W. H. Lewis, Oak Ridge National

Laboratory, June 1959. (Unpublished.)

10. Oak Ridge National Laboratory, June 1959. (Unpublished.)

11. F. L. Culler et al., Oak Ridge National Laboratory, Sept. 22, 1959. (Unpublished.)

12. Oak Ridge National Laboratory, Oct. 6, 1959. (Unpublished.)

13. J. O. Blomeke, H. E. Goeller, and W. H. Lewis, Oak Ridge National Laboratory, July 1959. (Unpublished.)

14. *Reactor Fuel Processing*, 2(3): (July 1959).

15. F. L. Culler, Oak Ridge National Laboratory, Sept. 30, 1959. (Unpublished.)

16. T. A. Gens, G. A. West, and L. M. Ferris, Oak Ridge National Laboratory, Aug. 24, 1959. (Unpublished.)

17. C. E. Stevenson, Phillips Petroleum Co., July 1959. (Unpublished.)

18. C. E. Stevenson, Phillips Petroleum Co., September 1959. (Unpublished.)

19. W. E. Shuler, Processing of Fuel Assemblies that Contain Zirconium, DP-335, January 1959. (Unclassified AEC report.)

20. E. S. Occhipinti, comp., Processing of Power Reactor Fuels, Quarterly Progress Report No. 6 for Jan. 1 to Apr. 1, 1959, DP-393. (Unclassified AEC report.)

21. R. G. Hart, A Review of the Chemical Aspects of Aqueous Processing, CRDC-822 (AECL-853), July 1959. (Unclassified Canadian report.)

22. *Reactor Fuel Processing*, 2(1): (January 1959).

23. H. E. Henry, Electrolytic Dissolution of Stainless Steel, DP-396, July 1959. (Unclassified AEC report.)

24. C. E. Stevenson, Phillips Petroleum Co., Sept. 14, 1959. (Unpublished.)

25. *Reactor Fuel Processing*, 2(4): (October 1959).

26. J. J. Shefcik and A. M. Platt, Preliminary Darex Flowsheet, HW-58600, Dec. 18, 1958. (Unclassified AEC report.)

27. J. E. Mendel and W. W. Schulz, Removal of Chloride Ion from Darex Process Dissolver Solution, HW-59033, Jan. 12, 1959. (Unclassified AEC report.)

28. B. C. Finney and F. G. Kitts, Darex Processing APPR Fuel: Effect of Acidity and Gas Sparging on Rate of Chloride Removal from Dissolver Product During Refluxing, ORNL-2753, Aug. 7, 1959. (Unclassified AEC report.)

29. J. L. Matherne, PRFR Pilot Plant: An Evaluation of Equipment Performance During the Processing of Irradiated Natural Uranium in April 1959, CF-59-9-49, Sept. 15, 1959. (Unclassified AEC report.)

Solvent Extraction

Modifications of Redox and Purex Processes

The established solvent-extraction processes, Redox and Purex, represent considerable investment in plant and technology. Work continues in an effort to improve these processes. Modifications of these processes are being sought to adapt them to the processing of a wide variety of nonproduction reactor fuels. These modifications seek to accommodate the poor resistance of the Redox extractant, methyl isobutyl ketone, to high acid conditions and the poor extraction efficiency of the Purex extractant, tributyl phosphate (TBP) diluted with kerosene, in other than nitrate media.

The previous Review[1] mentioned benefits obtained by operation of the product stripping columns with the organic phase continuous in the conventional Purex processing of irradiated normal uranium. These included significant improvements in column capacity and in decontamination of uranium and plutonium product streams. Data now available show that these benefits of organic-continuous operation were obtained without adverse effect on product recoveries. The ORNL pilot plant processed 12.5 tons of irradiated uranium with the organic phase continuous in the co-decontamination and the final uranium extraction cycles. Product recoveries for uranium and plutonium were 99.3 and 99.7 per cent, respectively.[2]

Work continues on the development of a flow sheet for the Consolidated Edison ceramic (UO_2-ThO_2) fuel. The interim flow sheet, for the extraction of uranium only with 2.5 per cent TBP, provided satisfactory levels of decontamination of better than 10^5 for ruthenium, zirconium-niobium, and rare earths. Uranium losses were less than 0.01 per cent. Tests of an acidic Thorex flow sheet using 30 per cent TBP in kerosene (Amsco) gave excessive thorium losses of 0.2 per cent.[3]

The Thorex process normally employs acid-deficient conditions to avoid third-phase formation. Interest is developing in decalin, as a Purex diluent, to take advantage of its 50 per cent higher solubility for the thorium-TBP complex. An additional advantage of decalin is elimination of the need for an aluminum nitrate salting agent. Apparently anomalous decontamination results have been reported for testing of the Thorex flow sheet with 42.5 per cent TBP in decalin. It does appear, however, that decontamination factors comparable to those realized under the conventional Thorex process are possible.[4-6]

Radiophosphorus-tagged TBP was used to study the fate of small amounts of TBP soluble in the aqueous phase in the Thorex process. The solubility of TBP in the aqueous phase was $1.08 \times 10^{-3} M$. The solubility of TBP degradation products was $7 \times 10^{-5} M$. Some 93 per cent of the TBP in the aqueous phase was removable by two-tenth volume washes with kerosene. Steam distillation netted an 88 per cent removal.[5]

Studies of Alternate Extractants

The limitations of the Purex and Redox processes emphasize the need for alternate extractants to meet the separations requirements of the nonproduction reactor fuels. To meet these needs, a wide variety of organonitrogen and organophosphorous compounds are being studied. The properties of these compounds include amazing selectivity and extraction power over a wide range of chemical conditions and, in many cases, resistance to radiation damage equal to or better than tributyl phosphate. The first production application of the organonitrogen and organophosphorous compounds was in the recovery of fertile values from ores. The established ore-processing solvent-extraction processes are called Amex and Dapex. Process development continues in these areas. Much of this work is relevant to the processing problems of nonproduction reactor fuels.

Phase separation difficulties in Amex and Dapex processing with the aqueous phase continuous have been traced to the presence of silicon. In mixing tests with Rohm and Haas 9D-178 amine or trilauryl amine contacted with an aqueous phase containing silicic acid, emulsion stability was dependent on the anion present in the order sulfate, chloride, and chlorate. It was postulated from the experimental evidence that the silicic acid stabilized oil in water emulsions by forming links between the oil droplets through the intervening aqueous phase. These links were presumed to form by bonding of silicic acid hydrogen atoms to electron donor groups provided by the amine anion oxygen atoms. This theory was supported by tests of the effect of organic additives containing active hydrogen atoms. These compounds effected a marked decrease in the time required for phase separation. These phase separation difficulties were not observed with water in oil systems; hence, where practical, organic-continuous operation would be preferable.[7]

Uranium can be extracted from carbonate solutions with a number of quaternary ammonium compounds. However, the phase separation characteristics of these systems is poor. Promising results were obtained with a new commercial mixture of ammonium compounds, Aliquot 336. The phase separation properties of the system were much improved. Some depression of extraction efficiency was noted, especially in the region of high uranium loading. Sulfate in the carbonate feed lowered the extraction coefficients, and the presence of fluoride or nitrate resulted in much poorer extraction efficiency. Dilute solutions of chloride and nitrate were effective stripping agents.[8]

A process is being developed for the recovery and separation of uranium and thorium from monazite sulfate liquors. Encouraging results were obtained in the development of a two-cycle process by capitalizing on the peculiar extraction characteristics of amine extractants. Primary amines have tremendous affinity for thorium; tertiary amines are very poor thorium extractants; and secondary amines exhibit intermediate performance. Batch studies of a number of $0.1M$ primary amines showed extraction coefficients as high as 1000. Tertiary amines showed negligible extraction coefficients for thorium, but uranium extraction coefficients as high as 50 were obtained with n-benzyl-1-(3-ethylpentyl)-4 ethylactyl amine. Satisfactory thorium stripping was accomplished with a number of reagents, the most effective of which was $3M$ nitric acid.[9] The two-cycle flow sheet was demonstrated using $0.05M$ triisoctyl amine diluted with 97 per cent kerosene – 3 per cent tridecanol to extract uranium in the first cycle. Thorium was recovered from the uranium-free liquor with $0.10M$ Primene JM diluted with 97 per cent kerosene – 3 per cent tridecanol. More than 99.9 per cent of the thorium was extracted in four stages with a uranium contamination of less than 10 ppm. Tests indicated that either uranium or thorium could be recovered in the first cycle with little contamination from rare earths or phosphate.

It was noted in the early stages of the study of organophosphorous and organonitrogen extractants that the solubility of the metal-extractant complex in the kerosene diluent was frequently quite low. Exceeding this low solubility resulted in the formation of a second organic phase. The addition of a long-chain alcohol increases the miscibility of solvent and diluent. The alcohol also improves the phase separation characteristics of the system. An alcohol often used for this purpose is tridecanol.

The selectivity of $0.08M$ Primene JM (amine) for thorium over rare-earth and iron contaminants was greatly improved by the addition of a long-chain alcohol to the kerosene diluent. One study reported decreases in the extraction of Ce(III) and Fe(III) by factors of 6 and 10, respectively, by the addition of 15 per cent tridecanol. The thorium extraction coefficients were virtually unaffected.[3]

In studies of the recovery and separation of uranium and thorium in $1.5M$ to $9.0M$ nitric acid with trialkyl phosphates and dialkyl phosphonates, the best results were obtained using phosphates and phosphonates with secondary alkyl side chains. Separation factors were 5 to 40 times greater than those obtained with TBP. Phosphonates with straight alkyl chains demonstrated poorer performance than TBP.[10,11] Some selected data appear in Table III-1.

The decladding of stainless-steel fuel elements in sulfuric acid results in a significant loss of fuel. A number of solvent-extraction systems are being tested for the recovery of uranium, plutonium, and thorium from sulfate decladding solutions. Good results have been obtained with primary amines and organophosphoric acids. Primary amines are strong ex-

Table III-1   EFFECTIVENESS OF NEUTRAL
ORGANOPHOSPHOROUS COMPOUNDS FOR
RECOVERY AND SEPARATION OF URANIUM
AND THORIUM IN NITRATE[11]

Compound*	Uranium extraction coefficient†	Uranium–thorium separation factor
TBP‡	17	11
DOPP‡	14	700
D(2EH)EHP‡	420	20
DBBP‡	460	12

* Extractants $1M$ in kerosene diluent.
† Aqueous phase $2M$ in HNO_3 and $0.002M$ in metal ion.
‡ TBP = tributyl phosphate.
  DOPP = di(octy(-2)phenyl phosphonate).
  D(2EH)EHP = di(2-ethylhexyl)2-ethylhexyl phosphonate.
  DBBP = dibutylbutyl phosphonate.

tractants for tetravalent uranium and plutonium. Since U(IV) and Pu(IV) do not ordinarily exist together in solution, a two-cycle flow sheet has been proposed. U(IV) is extracted first, after which sufficient ferric ion is added to stabilize Pu(IV) for extraction in the second cycle.[10]

Excellent recovery of U(IV) from $3M$ sulfuric acid was realized with $0.1M$ Primene JM. At low uranium concentrations the extraction coefficient was estimated at about 10,000. Extraction coefficients for Pu(IV) at aqueous-phase concentrations of 10 to 20 mg/liter were 1000 for $0.1M$ Primene JM and 4000 for $0.4M$ Primene JM.[11,12] Extraction of 99.5 per cent of the uranium and plutonium from decladding solution was accomplished with $0.3M$ Primene in 85 per cent kerosene–15 per cent tridecanol. Stripping with $5M$ nitric acid removed all but 3 per cent of the uranium and 0.1 per cent of the plutonium from the amine extractant. These data were obtained using an aqueous feed containing $2M$ sulfuric acid, 3 g of uranium per liter, and 0.5 mg of plutonium per liter.[8]

Dialkyl phosphoric acids can be used to extract uranium from sulfuric acid decladding solution. Tests of a synergistic mixture of di-2-ethylhexyl phosphoric acid (D2EHPA) and TBP gave uranium recoveries of greater than 95 per cent. About 2 per cent of the thorium present was also extracted. In the presence of an oxidant, D2EHPA will extract Pu(IV) from $2M$ to $3M$ sulfuric acid solution but Fe(IV) is also extracted.[8]

Tertiary amines have been successfully applied to the problem of recovering uranium and plutonium from a variety of metal ions. Distribution data were obtained for the system tri-isononylamine (TNA) in xylene–nitric acid. A small amount of a long-chain alcohol was required to prevent the formation of a second organic phase. Nitric acid was readily extracted with $0.262M$ TNA. The nitric acid concentration in the organic phase varied from $0.678M$ to $0.355M$ as the aqueous-phase nitric acid concentration was varied from $10M$ to $2M$. A linear relation was noted between TNA and uranium concentration in the organic phase. It was postulated that the addition compound $TNA-HUO_2(NO_3)_3$ was formed. With plutonium, less precise results were obtained. The plutonium distribution coefficient increased with increasing nitric acid concentration. Third-phase formation was noted at plutonium to TNA ratios greater than 0.5. One of the two organic phases was found to be essentially pure xylene. The data indicate that the plutonium extract might be $TNA-HPu(NO_3)_5$. Data were obtained on the separation of uranium and plutonium in $6M$ nitric acid. The distribution coefficients of both elements were affected by the presence of the other element. Relative enrichment of the plutonium in the TNA extractant was favored. Stripping of plutonium from the organic phase was difficult.[13]

Some work has been reported on the extraction of plutonium and neptunium by amines and organophosphorous compounds. This work is applicable to the processing of irradiated neptunium and the recovery of trace values from waste streams. In tests of di-n-butylbutyl phosphonate (DBBP) for extracting neptunium from synthetic Purex waste, losses were 0.1 and 0.4 per cent in the aqueous and organic phases, respectively. Decontamination factors were 2 from plutonium, 12 from thorium, 95 from zirconium, and 100 from ruthenium.[14]

Organophosphorous compounds were investigated as extractants for zirconium from nitric acid solutions containing fluorides. With most reagents tested, a precipitate formed in the organic phase. Satisfactory results were obtained with $0.43M$ trioctylphosphine oxide (TOPO) in carbon tetrachloride. Data were obtained for extraction from $7M$ nitric acid solution initially $0.25M$ to $0.5M$ in zirconium at a 2 to 1 fluoride to zirconium mole ratio. In six batch contacts, 94 per cent of the zirconium was extracted.[15]

Solvent Degradation

Degradation of process extractants and diluents leads to the formation of objectionable products which hinder contactor performance and extraction efficiency.

A major degradation product of TBP is dibutyl phosphate. Data are now available on the solubilities of uranium, zirconium, and aluminum dibutyl phosphate in a variety of solvents. As shown in Table III-2, all complexes showed

Table III-2   SOLUBILITY OF DBP COMPLEXES[15]

Solvent	Solubility of complex, g/liter		
	U–DBP	Zr–DBP	Al–DBP
H_2O	0.2	0.0	0.2
$1.5M$ HNO_3	1.32		1.0
$3.25M$ TBP in Amsco	0.9	3.6	0.3

appreciable solubility in a TBP-kerosene (Amsco) extractant. Extraction coefficients at DBP concentrations to $10^{-3}M$, determined under Purex acid conditions with $3.25M$ TBP in kerosene (Amsco), were 0.018 for zirconium and 2.4 for uranium. Under acid-deficient conditions the zirconium distribution coefficient increased to 1.0 at a DBP concentration in the organic phase[15] of $10^{-2}M$.

In other studies a general equation was derived to calculate the total radiation dose received by solvent in a pulsed column, assuming ideal mixing of the organic and aqueous phases. Methods were presented for using the calculated radiation dose to estimate the amount of TBP decomposed in a Purex first-cycle extraction column.[16]

Fundamental Solvent-extraction Studies

Complete data are now available on the results of isotopic exchange rate measurements to investigate the mechanism of uranium transfer between water and TBP. The experiments were performed in an hourglass-shaped vessel with a stable fixed-area interface. Briefly summarized, the results were as follows:

1. The transfer rate from aqueous to organic of both uranyl nitrate and nitric acid was second order with respect to the transferring solute.

2. Solute transfer from organic to aqueous was first order with respect to solute concentration and independent of the TBP concentration.

3. On the basis of an estimated activation energy of 3 kcal for transfer in either direction, the rate limiting factor was suggested to be physical rather than chemical.[17]

A photographic method is reported for measuring the resistance of an aqueous-organic interface to molecular diffusion. Uranyl ion concentration gradients were determined by photographically recording the transmittance of monochromatic light at an angle normal to the assumed direction of the concentration gradient. The uranium concentration at any point in a diffusion cell was taken as a linear function of the logarithm of the silver density on the exposed photographic plate.[18]
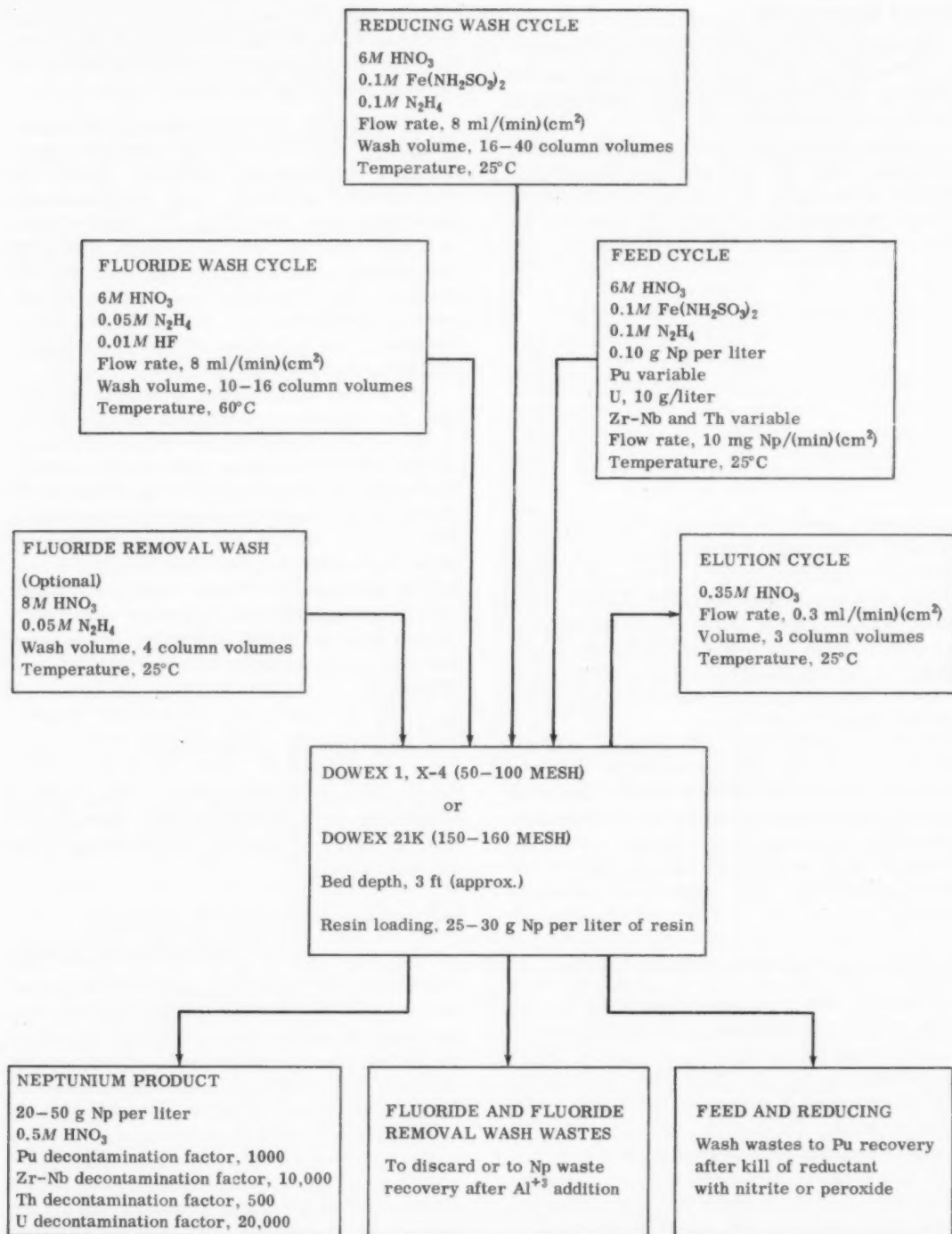
Another set of empirical equations is available for calculating equilibria in the uranyl nitrate−nitric acid−water−TBP-in-kerosene system. These equations, developed by ORNL, are based on the generally accepted extraction mechanisms, namely, uranyl nitrate extraction with 2 moles of TBP and nitric acid extraction as an equimolar complex. These equations have been programmed for digital computer solution. Good agreement between calculated and experimental data was noted except for low concentrations of TBP and high concentrations of uranium.[19]

Ion-exchange Processes

Ion-exchange processes have been applied to recovery of neptunium, uranium, and rubidium and to the identification of ruthenium from process solutions.

Ion-exchange Processes for Recovery and Purification of Uranium

Previous Reviews[1,20,21] have discussed recovery and purification of uranium by ion exchange. In recent work at ORNL[22] the effect of varying the total sulfate concentration on the kinetics of the absorption of uranyl sulfate on Dowex 21K at a uranium concentration of $0.0058M$ was studied in a series of runs using a stirred bath containing enriched uranium. The apparent diffusion coefficient calculated from a simple diffusion model remained within the range 1.25 to 1.3×10^{-7} cm^2/sec over a range of total sulfate concentrations from $0.026M$ to $0.20M$. The data indicate that the simple diffusion model probably is inadequate at small

REDUCING WASH CYCLE

$6M$ HNO_3
$0.1M$ $Fe(NH_2SO_3)_2$
$0.1M$ N_2H_4
Flow rate, 8 ml/(min)(cm^2)
Wash volume, 16—40 column volumes
Temperature, 25°C

FLUORIDE WASH CYCLE

$6M$ HNO_3
$0.05M$ N_2H_4
$0.01M$ HF
Flow rate, 8 ml/(min)(cm^2)
Wash volume, 10—16 column volumes
Temperature, 60°C

FEED CYCLE

$6M$ HNO_3
$0.1M$ $Fe(NH_2SO_3)_2$
$0.1M$ N_2H_4
0.10 g Np per liter
Pu variable
U, 10 g/liter
Zr-Nb and Th variable
Flow rate, 10 mg Np/(min)(cm^2)
Temperature, 25°C

FLUORIDE REMOVAL WASH

(Optional)
$8M$ HNO_3
$0.05M$ N_2H_4
Wash volume, 4 column volumes
Temperature, 25°C

ELUTION CYCLE

$0.35M$ HNO_3
Flow rate, 0.3 ml/(min)(cm^2)
Volume, 3 column volumes
Temperature, 25°C

DOWEX 1, X-4 (50—100 MESH)

or

DOWEX 21K (150—160 MESH)

Bed depth, 3 ft (approx.)

Resin loading, 25—30 g Np per liter of resin

NEPTUNIUM PRODUCT

20—50 g Np per liter
$0.5M$ HNO_3
Pu decontamination factor, 1000
Zr-Nb decontamination factor, 10,000
Th decontamination factor, 500
U decontamination factor, 20,000

FLUORIDE AND FLUORIDE
REMOVAL WASH WASTES

To discard or to Np waste
recovery after Al^{+3} addition

FEED AND REDUCING

Wash wastes to Pu recovery
after kill of reductant
with nitrite or peroxide

Figure 1—Neptunium purification flow sheet.[24]

values of contact time. Experiments with various stirrer speeds showed that the liquid film resistance to diffusion could be safely disregarded in this series of experiments. Jury and Adams[23] have studied the system Dowex 21K and aqueous uranyl sulfate solution in the solution composition range: $0M$ to $0.005M$ uranyl sulfate, $0.15M$ total sulfate, $0.02M$ sulfuric acid (pH 2). It is shown that UO_2SO_4 and/or $UO_2(SO_4)_2^{-2}$ are sorbed on the resin to form $R_2UO_2(SO_4)_2$. It is surmised that these same species are also involved at higher uranyl concentrations at pH 2. Above pH 2 it is suggested that $U_2O_5SO_4$, $U_2O_5(SO_4)_2^{-2}$, and $R_2U_2O_5SO_4$ species may be involved.

The apparent uranium diffusion coefficient in 1200-μ beads of Dowex 21K anion-exchange resin was approximately 1.3×10^{-7} cm^2/sec with a $0.0029M$ uranium loading solution, the same as that with a $0.0058M$ solution.[4] However, with the latter solution and 960-μ beads, the apparent coefficient was 0.76×10^{-7} cm^2/sec. This discrepancy may be partly due to a difference in the physical or chemical properties of different size fractions of the resin or to experimental error. The self-diffusion coefficient of sulfate ions in Dowex 21K was 1.2×10^{-6} cm^2/sec for 1200-μ beads.

Volumetric distribution coefficients for U(IV) and Pu(IV) on weakly basic polyamine resins in $3M$ sulfuric acid were 4.5 and 8.5, respectively.[10] Equilibrium loadings of U(IV) on Dowex 21K from $0.025M$ to $0.6M$ sulfate solutions at pH 2 were fitted by Langmuir sorption isotherms, with initial slopes approximately inversely proportional to the sulfate concentration, which extrapolated to a maximum loading of 1 mole of uranium to about 4.8 moles of resin.

Concentration and Final Purification

of Neptunium by Ion Exchange

It was demonstrated by Ryan[24] that Np(IV) can be readily absorbed onto anion-exchange resins from $6M$ nitric acid containing ferrous sulfamate and hydrazine or semicarbazide; separated from plutonium, uranium, and common metallic impurities by washing the resin at $25°C$ with $6M$ nitric acid containing ferrous sulfamate and hydrazine or semicarbazide; separated from fission products and thorium by washing the resin at $60°C$ with $8M$ nitric acid$-0.01M$ hydrofluoric acid containing hydrazine or semicarbazide; and eluted at concen-

trations greater than 40 g of neptunium per liter with $0.35M$ nitric acid at $25°C$ (see Fig. 1 for flow sheet). Decontamination factors of greater than 10,000 from uranium, plutonium, and common metallic contaminants, greater than 25,000 for fission products normally expected in the feed (mainly zirconium-niobium with some ruthenium-rhodium), and greater than 1000 for thorium are obtainable under proper operating conditions.

Because of (1) low processing rates, (2) ability to carry out the absorption cycle at $25°C$, and (3) absence of radiation damage problems, the Dowex 1, X-4 (50 to 100 mesh) resins are considered the best choices for this application. Gassing occurs with the use of ferrous sulfamate–semicarbazide reductant but is not a serious problem and does not occur with ferrous sulfamate–hydrazine reductant in $6M$ nitric acid.

Miscellaneous Ion-exchange Studies

Some aspects of the anion-exchange behavior of uranyl nitrate in the presence of other inorganic nitrates have been examined by Foreman et al.[25] They found that the addition of inorganic nitrates to aqueous solutions of uranyl nitrate enhances the uptake of uranium on the anion-exchange resin Deacidite FF in the order aluminum > calcium > lithium > ammonium. The predominating cause is considered to be the facilitation of formation of nitrate complexes by the uranyl ion, and of the subsequent ion exchange, due to the decrease in the effective water content of the system resulting from hydration of the added cation. Visible absorption spectra revealed no new peaks ascribable to an anionic uranyl nitrate complex. The variation of the distribution coefficient of uranium with aluminum nitrate concentration is shown in Fig. 2.

Data indicating that the ruthenium species extracted from Purex feed are nitrate nitrosylruthenium compounds was presented by Pollock and Wallace.[26]

Amphlett et al.[27] have shown that rubidium and cesium may be efficiently separated in macroquantities on columns of zirconium phosphate, at loadings up to 10 per cent, by elution with solutions of ammonium salts or of nitric acid. High yields of pure materials are obtained if the separation is performed at elevated temperatures (57 to 83°C).
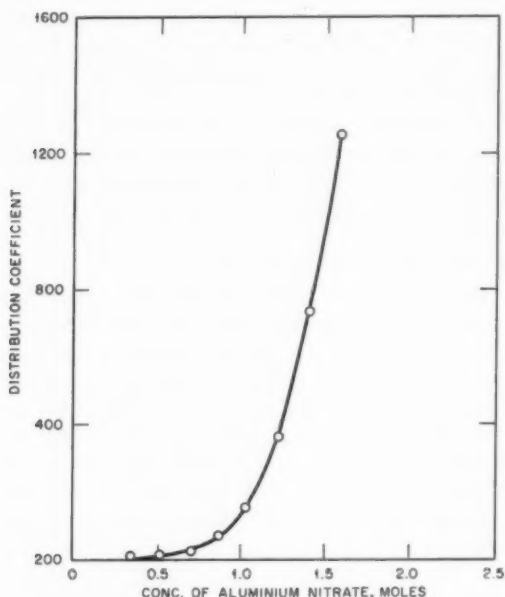
Figure 2 — Variation of distribution coefficient of uranium with aluminum nitrate concentration.[26]

Ion-exchange equipment development work is being actively pursued at ORNL and HAPO. Achievements at ORNL[10] include operation of continuous ion-exchange contactors at higher solution and resin flow rates, up to 3000 and 225 gal/(hr)(sq ft), respectively, and at higher solution to resin flow ratios, up to 1000/1, than heretofore demonstrated. Use of water-main pressure to move the resin, instead of using a pump or hydraulic accumulator as in the past, was demonstrated.

Preliminary studies[14, 17, 28] in a 3-in.-diameter 4-ft-long Weiss contactor indicated satisfactory resin flow and retention on each plate with various pulsing conditions and no fluid flow. The four-plate unit was then replaced by a 3-in.-diameter 3-ft-long column containing 15 resin support plates spaced 2.5 in. apart. The plates were equipped with $\frac{1}{2}$-in. downcomers extending 1 in. above and 2 in. below each plate. Shake-down runs with both water and 7M nitric acid indicate satisfactory resin retention at flow rates up to 3.5 gal/(min)(sq ft). Although the resin was partially fluidized at the maximum flow rate, the settled height remained constant at 1 in. on each plate (the distance the downcomers protruded above the plate). A uranium feed will be used in future runs to study the exchanging efficiency of the contactor.

Goren[29] has developed a process for recovery of poisoned ion-exchange resins. The resin is treated first with 42.5 per cent sulfuric acid for more than 15 hr, and then, after rinsing, the resin is treated with 10 per cent sodium hydroxide for 8 hr. Resin (type IRA-400) thus treated was restored to full operating capacity.

Volatility Processes

In fluoride volatility processing, uranium and plutonium are decontaminated and recovered from various types of fuels by fluorination to the volatile hexafluorides. A number of different fluorination agents and separation processes have been proposed. In this Review, progress in fused-salt processing and dry fluorination methods are reported, together with results of some liquid-vapor separations.

Fused Salt - Fluoride Volatility Process

Work at ORNL for the past year on the fused salt—fluoride volatility process for recovery of uranium hexafluoride from zirconium matrix fuels is included in the annual summary of the Chemical Technology Division.[10] Decontamination and dissolution results are summarized, and flow sheets and equipment are discussed. The principal problem in this process is one of minimizing corrosion in both the dissolution and fluorination steps. A pilot-plant hydrofluorinator (dissolver) has been fabricated from INOR-8 (a nickel-molybdenum alloy) with a wall corrosion allowance of 125 mils. A penetration rate of 25 mils/month during exposure to HF-NaF-LiF at an average temperature of 600°C is predicted, based on corrosion measurements of a draft tube in a prototype hydrofluorinator. Because of the large effect of temperature on corrosion rate, the initial and final dissolution temperatures have been decreased to 650 and 500°C, respectively. The lower dissolution temperature was accomplished by changing the initial melt composition from 57—43 mole % LiF-NaF (m.p. 652°C) to 25—37.5—37.5 mole % ZrF_4-NaF-LiF (m.p. 605°C). The melting point decreases as additional zirconium fluoride is produced by dissolution of the fuel. Uranium is fluorinated to hexafluoride in the range 450 to 500°C to minimize corrosion and to achieve maximum product decontamination.
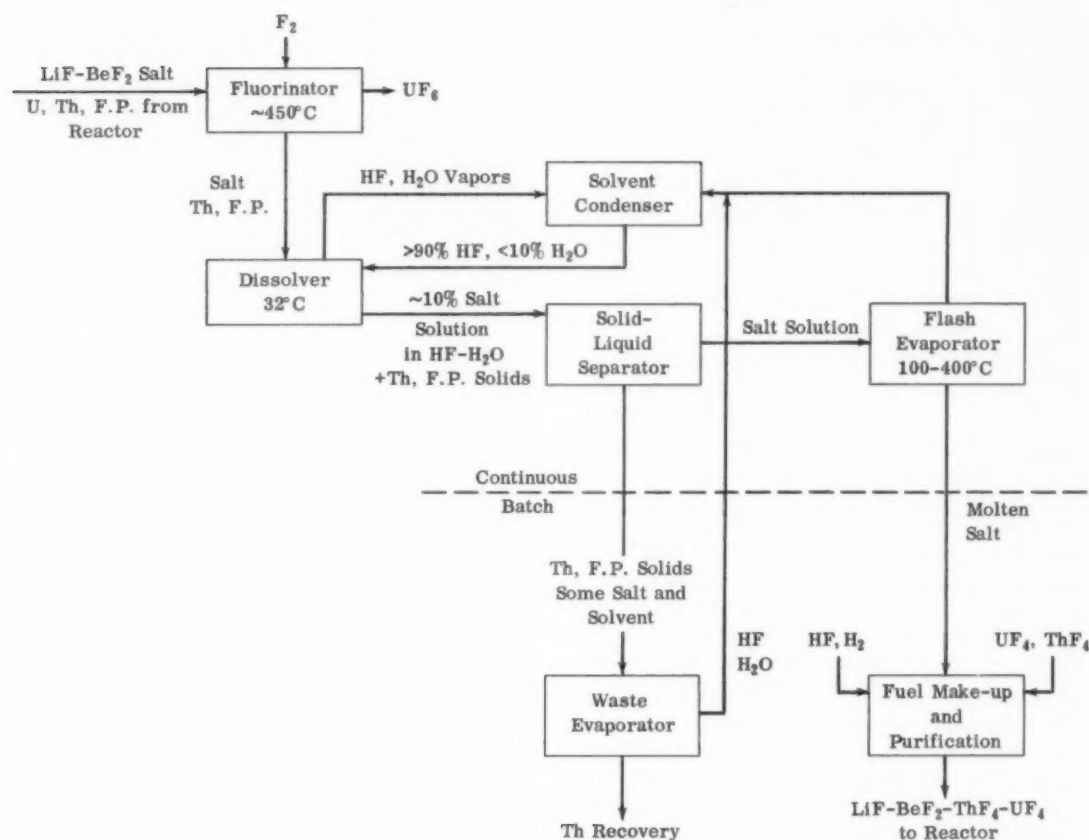
Figure 3 — Tentative flow sheet for fluoride volatility and HF dissolution of molten-salt reactor fuel.[10]

A series of tests was made at Argonne National Laboratory to examine the feasibility of spray fluorination as a means of contacting fused-salt-bearing uranium with fluorine.[30] In this scheme molten salt is fluorinated by spraying into a fluorine atmosphere. The salt is allowed to solidify before contacting the walls of the container, and the uranium hexafluoride formed is recovered from the gas phase. In a series of six tests at three different temperatures, the maximum uranium removed was 29 per cent with a fluorine temperature of 200°C. The initial composition of the salt tested was 1 wt.% uranium tetrafluoride added to 40 mole% zirconium tetrafluoride – 60 mole % sodium fluoride (m.p. approximately 505°C). Results were correlated in terms of droplet size and initial temperature difference between the droplet and the surroundings (which determines contact time of the molten salt and fluorine).

Smaller droplets and larger contact times favor more removal. From the correlated data obtained it was estimated that a four-stage process, i.e., four spray contacts with fluorine, would be required to give 99 per cent removal. The process was not considered attractive for scale-up.

Processing of Molten Salt

Power Reactor Fuel

Fuel processing methods are being investigated for molten-salt nuclear reactors which use lithium fluoride – beryllium fluoride salt as a solvent for uranium tetrafluoride and thorium fluoride.[10,31] A flow sheet is shown in Fig. 3. Uranium is separated and recovered from the molten salt by fluorination to hexafluoride at 450°C. For recovery of the thorium and lithium fluoride – beryllium fluoride solvent salt, which

is highly enriched in Li[7], a process based on dissolution of the solid salt in concentrated (~90 per cent) aqueous hydrofluoric acid is proposed. The solvent salt is separated from thorium and the major neutron poisons (rare earths and neptunium) which are insoluble in the nearly anhydrous hydrogen fluoride. Evaporation of a solution of salt in 90 per cent hydrogen fluoride, followed by fusion of the salt, regenerates the lithium fluoride−beryllium fluoride without significant hydrolysis. Thorium can be recovered by solvent extraction.

Solubilities of lithium fluoride and beryllium fluoride in aqueous 70 to 100 per cent hydrogen fluoride have been determined. The beryllium fluoride solubility is appreciably increased in the presence of water and large amounts of lithium fluoride. Salt solubilities of 150 g per liter are attainable. Tracer experiments indicate that rare-earth solubilities relative to lithium fluoride−beryllium fluoride solvent salt solubility increase from about 10^{-4} mole % in 98 per cent hydrogen fluoride to 0.003 mole % in 80 per cent hydrogen fluoride. Fluorination of uranium from lithium fluoride−beryllium fluoride salt was demonstrated. This appears feasible also for the recovery of relatively small concentrations of uranium produced in the lithium fluoride−beryllium fluoride−thorium fluoride blanket. Investigation of alternative methods that might simplify or improve the process has been started.

Direct Fluorination of Oxide Fuels

Considerable interest has developed in the use of ceramic fuels for power reactors. Fuels containing uranium and plutonium oxides may be processed in a simple and economic manner by a direct fluorination process, involving removal of the oxide fuel from the cladding, followed by treatment of the oxide by a fluorinating agent. Uranium and plutonium oxides are converted to the hexafluorides and volatilized. Separation and additional purification of the hexafluorides are followed by such chemical reactions as are necessary to convert the uranium and plutonium hexafluorides to the final desired compounds. The simultaneous reduction and pyrohydrolysis of uranium hexafluoride may serve as a simple means of converting the uranium back to the oxide for use in the fuel.[32]

Exploratory experiments have been carried out to determine the rates of fluorination of

uranium dioxide samples with thermal histories similar to those anticipated for reactor fuel pellets.[30] Samples of uranium dioxide were fluorinated with a stream of fluorine in a heated tube furnace. Uranium hexafluoride formed in the reaction was removed from the gas stream by two cold traps, and the amount collected was determined. Rate data for the fluorination of several types of samples are shown in Table III-3. The rates of fluorination of the fused and

Table III-3   FLUORINATION OF FUSED AND SINTERED URANIUM DIOXIDE PELLETS[30]

(Fluorine pressure: 1 atm, 100% F_2)
(Flow rates: 50 to 70 cm^3/min; constant for each experiment)

Initial area, cm^2	Temp., °C	Rate,* mg U/$(cm^2)(hr)$
1.06	375	58.5†
1.51	500	2280†
1.66	600	2820†
1.87	500	3190‡
2.59	500	2500§

*Based on initial geometric area of sample.

†These samples were pieces of arc-fused UO_2 having smooth faces.

‡Pressed and sintered UO_2 pellet (fuel grade), hydrogen fired at 1825°C for 12.5 hr, 78 per cent of theoretical density.

§Pressed and sintered UO_2 pellet (fuel grade), hydrogen fired at 1340 to 1400°C for 16 hr, 63 per cent of theoretical density.

ground uranium dioxide were appreciably less than that found for material produced by hydrogen reduction of uranium trioxide at lower temperatures.[1] X-ray analysis of the unfluorinated residue showed that conversion to uranyl fluoride and uranium tetrafluoride occurs simultaneously with formation of uranium hexafluoride. From the preliminary data it appears that undiluted uranium dioxide fuels will react with elemental fluorine at rates acceptable for process use.

A complete knowledge of the reaction $PuF_4(s) + F_2(g) = PuF_6(g)$ is needed for the development of the fluoride volatility process for the recovery of fissile materials from fuels containing plutonium. In a continuing study[31] of the equilibrium constant for the above reaction, measurements at 300°C gave a mean value of $K_p = K_c = (PuF_6)/(F_2) = 0.0026$.

Kinetic Studies of the Fluorination
of Uranium Tetrafluoride

The formation of uranium hexafluoride by dry fluorination of the tetrafluoride is the most important current method. At the Capenhurst Works in England, basic kinetics data have been reported.[33,34] The reaction between uranium tetrafluoride and fluorine was studied between 265 and 348°C by following the change in weight of the solid phase as a thin layer of ground material, using a spring thermobalance. Formation of uranium hexafluoride at the solid surface is accomplished by migration of fluorine ions into the uranium tetrafluoride lattice. The rate of production of uranium hexafluoride is in agreement with the kinetics expected for reaction between a gas and a solid at a continuously diminishing spherical interface. The rate of reaction depends on the temperature, no reaction being detectable below 220°C. Within the limits of experimental accuracy, the Arrhenius equation relates the reaction-rate constant, and the preparations of uranium tetrafluoride were 15.5, 19.1, and 19.9 kcal/mole. A linear relation is shown to exist at 1 atm total pressure between the reaction rate and concentration of fluorine in the range 10 to 100 per cent, but within the range examined the reaction rate is not affected by the velocity of gaseous reactant past the solid. The rate of uranium hexafluoride production is dependent on an "effective" surface area of uranium tetrafluoride rather than the surface area determined by gaseous adsorption; this is consistent with the notion that the internal surface of pores is less available for the reaction. It is believed that the mechanism is direct rather than one involving intermediate fluoride compounds; no initial weight increases were noted, such as would result from the formation of intermediate compounds. The values of activation energy here reported are supported by those obtained at ANL and previously cited.[14]

The reaction between uranium tetrafluoride and chlorine trifluoride was studied[34] between 17 and 193°C, using the same basic technique as described above for the investigation of the uranium tetrafluoride–fluorine reaction. The mechanism and kinetics of reaction were shown to be substantially the same for chlorine trifluoride as fluorine. The reaction rate passes through a maximum at 105°C, falls to a minimum at 148°C, and then rises again. An explanation of this unusual behavior is suggested by the authors in terms of the thermal stability of intermediates.

In the regions 17 to 58°C and 156 to 194°C, within the limits of experimental accuracy, the Arrhenius equation relates the reaction-rate constant and the temperature of reaction; the activation energies determined for uranium tetrafluoride prepared by hydrofluorination were 5.6 and 3.4 kcal/mole for the above two temperature zones, respectively. A linear relation is shown to exist near ambient temperature between the reaction rate and partial pressure of chlorine trifluoride. In the velocity range examined, gas velocity had no effect on the reaction rate. Compared with the uranium tetrafluoride–fluorine reaction, the fluorination with chlorine trifluoride proceeds at a much lower temperature and has a lower activation energy.

Vapor-liquid Equilibrium in the System Bromine Pentafluoride - Uranium Hexafluoride

Bromine fluorides constitute a group of relatively high-boiling liquid fluorinating agents. Of these, bromine pentafluoride is the most stable and the one with the closest boiling point to uranium hexafluoride. Distillation is a convenient means of separation of these materials. Data on the vapor-liquid equilibrium for this system were recently published.[35]

The vapor pressure of bromine pentafluoride, at temperatures above its boiling point, is given by the equation

$$\log_{10} P_1^0 = 6.4545 - 0.001101t - \frac{895}{t + 206}$$

where $P_1^0 = $ mm Hg, $t = $ °C. The values for the vapor pressure of bromine pentafluoride predicted by this equation were checked to within ±0.5 per cent at four temperature levels in the range 61.3 to 89.4°C. The compressibility factors of saturated vapor mixtures of bromine pentafluoride and uranium hexafluoride were found to be 0.936 at 70°C and 0.917 at 90°C. These values are in excellent agreement with the values predicted from Berthelot's equation of state and from generalized correlations in terms of reduced properties. It was found that measurement of the vapor density of saturated uranium hexafluoride–bromine pentafluoride mixtures could serve as a useful technique for

the determination of composition to within ±1 per cent.

To obtain reliable data on the vapor-liquid equilibria in the system bromine pentafluoride – uranium hexafluoride, it was found necessary to introduce elemental fluorine into the system to the extent of about 10 mm Hg partial pressure to ensure that extraneous chemical species such as bromine, bromine monofluoride, and bromine trifluoride were not formed. The data shown in Fig. 4 for the vapor-liquid equilibrium at 90°C
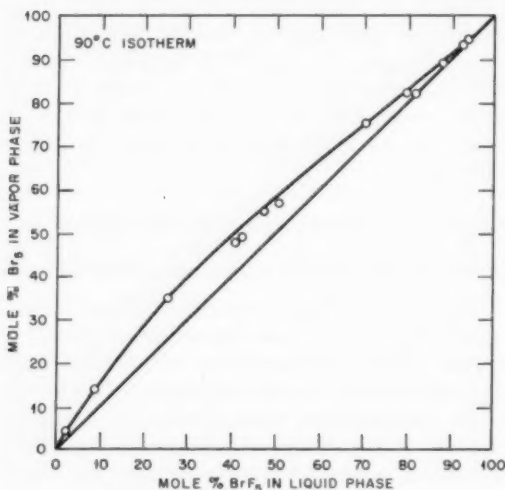

Figure 4 — Vapor-liquid equilibrium for the system bromine pentafluoride – uranium hexafluoride.[35]

are typical of the data obtained. Comparisons made with published results on distillation of the binary, condensed equilibria, and the theory of regular solutions all indicate that the bromine pentafluoride – uranium hexafluoride system shows small positive deviations from ideality with no azeotrope. Discussion is presented of points of difference in this work with that of Ellis and Johnson previously cited.[21]

Miscellaneous

A laboratory study of the reaction between uranium hexafluoride and uranium dioxide has been made.[36] Although the mechanism was not rigorously determined, experimental evidence supports the following net reaction near 500°C:

$$UO_2 + UF_6 \rightarrow UO_2F_2 + UF_4$$
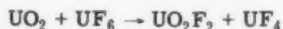
Karbate anodes for fluorine cells have been tested in production service at the Oak Ridge Gaseous Diffusion Plant.[37] These anodes have increased the average life of 4000-amp fluorine cells by 32.7 per cent as compared to those using grade YBD carbon anodes. The mechanism of failure of electrodes is by breaking or cracking. The average service life of 64 cells using Karbate anodes was 12.58 million ampere-hours. Karbate anodes are produced by impregnating YBD carbon anodes with a phenolic resin. Resin content of 9 to 10 per cent gives electrodes of the best over-all properties. Disadvantages of the Karbate anodes are (a) slightly more difficult initial depolarizing, (b) 0.4- to 0.8-volt higher voltage operation initially, and (c) a cost of an additional $3 per anode for impregnation. The over-all saving of the Karbate anodes is, however, substantial.

A number of patents have recently been issued on matters pertaining to fluoride volatility processing. One patent[38] describes an improved process for selectively recovering plutonium from a solution containing fission products, together with precipitated cerium trifluoride added for effecting carrier precipitation of plutonium. The resulting carrier precipitate is dried and subjected to fluorination at about 600°C. The plutonium forms a volatile fluoride and is so separated from the nonvolatile cerium fluoride. A method has been patented[39] for the concentration and recovery of plutonium by fluorination and fractionation. The metallic mass containing uranium and plutonium is heated to 250°C and contacted by a stream of elemental fluorine. After fluorination of the metallic mass, the reaction products are withdrawn and subjected to distillation treatment to separate the fluorination products of uranium and to obtain a residue containing the fluorination products of plutonium. The separation of plutonium from uranium and/or fission products by formation of the higher fluorides of uranium and/or plutonium is described in another patent.[40] Neutron-irradiated uranium metal is first converted to the hydride. This hydrided product is then treated with fluorine at about 315°C to form and volatilize uranium hexafluoride, leaving plutonium behind. The plutonium may then be separated by reacting the residue with fluorine at about 500°C and collecting the volatile plutonium fluoride thus formed.

Pyrometallurgical Processing

Development of pyrometallurgical processes is under way at several atomic energy sites. Interest in these processes, some of which were considered in the early days of the Manhattan Project, has grown because they may provide reduction in fuel processing costs through ability to handle short-cooled fuels and the elimination of chemical conversions. Two announcements have been made by the AEC relative to work in the pyrometallurgical field:[41]

1. A one-year $216,000 contract has been awarded to the Dow Chemical Co. for research on the pyrometallurgical processing of irradiated fuel.

2. A $1 million contract has been awarded to W. A. Klinger, Inc., of Sioux City, Iowa, for the construction of a Metals Process Development Building at the Ames Laboratory, which is operated by Iowa State University for the AEC. The new facility will enable Ames to conduct "larger-than-laboratory" metal-process development research and provide space to carry out the Laboratory's pure-metals program for the AEC.

Melt Refining

The term melt refining refers to the purification of metal fuels which can be effected through fission-product removal by volatilization and formation of stable drosses by melting in ceramic crucibles.* Because of its simplicity, it is being incorporated into a pilot plant (called Fuel Cycle Facility) adjacent to the Experimental Breeder Reactor No. II (EBR-II), both of which are now under construction at Arco, Idaho, by Argonne National Laboratory. Ground was broken for the Fuel Cycle Facility[43] on July 30, 1959. As the first pyrometallurgical process to be demonstrated on a pilot-plant scale, the evaluation of technical feasibility and economics of this process will have a decisive

influence on the future of pyrometallurgical processes in general.

Because equipment will be operated in a high-gamma background (10^5 r/hr) and in a dry (<100 ppm water) argon–5 per cent nitrogen (maximum) atmosphere, many problems in selection of materials are encountered. The ANL Chemical Engineering Division quarterly reports[43,44] provide a record of progress in testing and evaluation of lubricants, gasket materials, windows, electric motor brushes, lights, paints, ceramics, and other materials in various atmosphere environments and at various irradiation levels.

The use of a special Shell irradiation-resistant grease is considered practical inasmuch as stiffening under irradiation did not begin until after 10^9 rads.[43] This is equivalent to about two years in the Fuel Cycle Facility. The useful life may be extended in an argon atmosphere. An alternative solution is the production, by an electrolyzing treatment, of hard corrosion-resistant surfaces which may wear well with little lubrication.

Mercury-vapor lamps (1000-watt) have been specified for use in the Facility.[43,44] It is of interest to compare the gamma-radiation stability of various types of bulbs. Table III-4 gives a

Table III-4 COMPARISON OF LIGHT OUTPUT AT VARIOUS INTEGRATED GAMMA EXPOSURES FOR THREE LAMPS[43]

Gamma exposure, rads (water)	Light output after irradiation, % of original intensity		
	175-watt white fluorescent (ASA Code H22KF/W)		400-watt clear-glass-envelope lamp (ASA Code H25HC)
	Lamp A	Lamp B	
1×10^6	98	98	95
1×10^7	98	98	88
1×10^8	97	97	60–65
2×10^8	97	97	60–65
5×10^8	97	97	60–65
8×10^8		85	60
1×10^9		83–85	50

comparison of the light output of three lamps operated continuously while in the gamma field. The 175-watt white fluorescent mercury-vapor lamps (having the same construction as the 1000-watt lamps) retained 80 to 85 per cent of their initial intensity at irradiation levels of up to 10^9 rads and showed marked superiority over
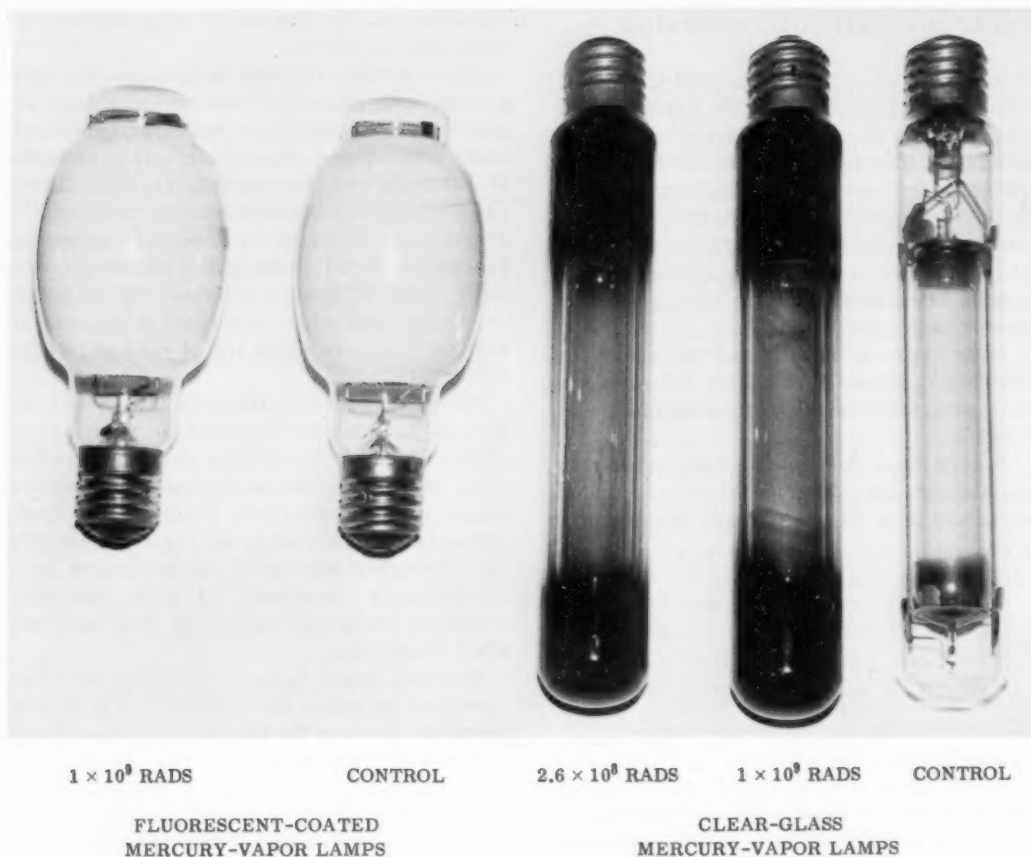
---

*Various modifications of slagging processes for purification of uranium are incorporated in a recently issued patent[42] filed for in April 1945. These include melting in graphite alone or in the presence of salts such as calcium fluoride and uranium tetrafluoride and improving separations by a combination of selective oxidation and volatilization effected by bubbling an argon-nitrogen mixture or a carbon tetrachloride-argon mixture through the melt.

1×10^9 RADS   CONTROL 2.6×10^8 RADS 1×10^9 RADS   CONTROL

FLUORESCENT-COATED   CLEAR-GLASS
MERCURY-VAPOR LAMPS   MERCURY-VAPOR LAMPS

Figure 5—Effect of gamma irradiation on mercury-vapor lamps.[43]

a lamp with a clear-glass envelope (see Fig. 5). It appears that the fluorescent coating has a beneficial effect in preventing or delaying darkening of the glass.

The shielding window for the Facility for processing and refabrication of fuel elements for the EBR-II has been described.[45] The window is designed for a gamma-radiation intensity up to 10^6 r/hr for 8 hr per day. Steel shutters will shield the window when it is not in use. The design reasons for the window configuration and the choice of materials are discussed. Operation of the plant in an inert atmosphere requires a gastight seal at the window aperture. The design details of the seal and test data on its performance are included. Data are also included on the computed light transmittance of the window before and after a 10^{10}-r exposure.

Reports continue to be issued describing equipment or equipment components on which work was done for the Pyrometallurgical Refabrication Experiment (PRE) for SRE type metallic reactor fuels, now discontinued. The development and demonstration of a special in-cell workbench for maintenance of radioactive PRE in-cell equipment have been described.[46] The bench (1) rotates, (2) moves in a vertical direction, (3) is remotely operable, and (4) has all in-cell components remotely maintainable.

Liquid Metal and Salt Processes

Liquid metals continue to show promise as processing media for various fuel materials. Increasing attention is being given to fused salt—liquid metal combinations. Such combinations

are convenient for selective oxidation and reduction reactions because of the solubility of salt and metal reactants and reaction products in their respective phases, because of the generally low mutual solubility of salts and metals which favors high separation factors, and because contacting of immiscible liquid phases is generally not difficult. The processes envisioned involve dissolution of the spent reactor fuel in an appropriate metal solvent, following which separations of fission products and other elements are effected by selective crystallization, or extraction into immiscible liquids (fused salts or metals). Recovery of the fissile elements from accompaning solvent metal is generally effected by vaporization of the latter.

Data on the properties of liquid-metal systems are being collected systematically to permit the design of separations processes and to furnish the basis for the evaluation of theories of liquid-metal solution. Recent additions to solubility data are those of barium and strontium in cadmium[47] and of palladium, ruthenium, and zirconium in zinc.[8] A study of solubility data of various metals in liquid-metal solvents is also in progress at Nuclear Metals in an attempt to establish general relations concerning solubility behavior. Additional thermodynamic data have also been reported for solutes in zinc and cadmium systems. These include activity coefficients of thorium, uranium, and zirconium in zinc; uranium in cadmium; and free energies of formation of the intermetallics.[43,48] A tentative plutonium-zinc phase diagram has been determined which indicates the existence of four intermetallic compounds,[49] $PuZn_2$, Pu_2Zn_9, $PuZn_8$, and Pu_2Zn_{17}.

Measurement of solute element solubilities in mercury is under way at ORNL[10] to determine process capabilities of a mercury solvent. Uranium solubility in mercury increased from 0.0067 to 1.18 wt.% as the temperature was increased from 40 to 356°C. Over the same temperature range, the solubility of thorium in mercury increased from 0.0021 wt.% to only 0.0295 wt.%. Because of these great differences in solubility, it was thought that a method of separation of uranium and thorium could be devised. However, extraction of uranium from thorium was incomplete because of coprecipitation of UHg_4 with $ThHg_3$.

At Ames a study is being made of the pyrometallurgical purification of uranium by oxidation or reduction reactions utilizing liquid zinc and KCl-LiCl eutectic as solvents, $ZnCl_2$ as an oxidant, and magnesium as a reductant.[48,50] It was found that excess zinc chloride oxidizes both uranium and cerium so that they move into the salt phase. Noble metals such as molybdenum remain in the metal phase. By equilibration with a zinc-magnesium alloy, the uranium and cerium may be transferred back into the zinc phase. By controlling the amount of magnesium present, the uranium is reduced preferentially and a uranium-cerium separation can be effected. Separation of uranium from other elements is also being determined. Uranium transfers to the metal phase from the salt phase were effected to the extent of 99 per cent. The behavior of protactinium is similar to that of uranium. Uranium concentrations in the zinc phase considerably in excess of the solubility of uranium in liquid zinc can be achieved by transferring the uranium into a saturated solution of uranium in zinc, thus continually precipitating the uranium as it transfers.

Dissolution of zirconium-based fuel elements by a salt-phase chlorination process has been proposed.[51] Scoping experiments in Pyrex equipment at 510 to 575°C have shown that lead chloride rapidly dissolves zirconium, Zircaloy-2, and uranium-zirconium alloys; that zirconium tetrachloride readily volatilizes from the melt; and that uranium loss by volatility can be reduced to a negligible amount. Salient advantages offered by the Alloy Reguline Chloride Oxidation (ARCO) process include early separation of matrix material simultaneously with dissolution, reduction in size of final uranium decontamination equipment, and compact waste storage.

The process has possibilities as a head-end step for an aqueous process or as a separate pyrochemical process. A major problem of plant scale will be that of containment material. Possibilities include molybdenum, carbon and chromium steels, graphite, porcelain, and alumina. However, the experiments have been sufficiently encouraging to justify continued exploration and initiation of allied programs in corrosion and equipment design.

The following reductions of thoria by aluminum at 1050°C in the presence of an AlF_3-LiF flux have been achieved at Atomics International:[52]

AlF$_3$ in flux, mole %	ThO$_2$ reduction, %
0	48
14.5 (eutectic)	82
25.7 (Li$_3$AlF$_6$)	80
52.8 (LiAlF$_4$)	59

A bibliography on molten salts[53] has been issued covering the work published in the technical press up to 1958. References have been classified under useful subject headings.

Oxide reductions by magnesium in metal solutions are employed in several processes under consideration for irradiated fuels and may also have important applications in raw materials production. Reduction of uranium oxide is being studied at ANL in connection with processing of crucible residues (skulls) from the EBR-II melt-refining process.[43] These will probably be partially or completely converted to oxides to facilitate removal from the crucible. (The nitridation characteristics of the skull material have also been studied since they will be exposed to a dilute nitrogen-argon atmosphere.) Reduction yields approaching 90 per cent have been realized at 650°C in cadmium—3 per cent magnesium solutions.

Amalgam processing of high-fired uranium dioxide fuels is being investigated at ORNL.[10] In two runs, 1700°C-fired uranium dioxide was reduced with magnesium amalgam at 1000°C under argon in the presence of magnesium chloride, with apparently 100 per cent reduction yield.

Development of engineering techniques and equipment which are necessary to the success of liquid-metal processes is under way at several sites. Construction of a large-scale distillation unit (100 kg of cadmium per hour) has been started at Argonne for study of distillation operations on a practical scale.[43] A number of other equipment components are also under development. These include retorting and phase separation equipment, freeze valves, remote connectors and unions, pumps, and liquid-level devices. Similar liquid-metal equipment development work is being carried out at Ames and Atomics International.

A mild steel loop in which a molten cadmium—1.5 per cent uranium alloy was circulated at 550°C by an electromagnetic pump was operated without incident for 1000 hr.[43] Examination of the loop did not indicate significant corrosion, but there are signs of slight interaction at three points. The performance of the loop and the mild steel containment material is encouraging, but further checking is indicated. Mild steel and 410 steel capsules were intergranularly attacked by cadmium—10 per cent zinc alloys at 700°C.

Processing of Ceramic Fuels

1. *Oxide Fuels*. Previous Reviews have contained information on chemical pulverization of sintered uranium dioxide as a step in the low-decontamination processing of such fuels. The laboratory-scale studies at Atomics International have been combined into a report[55] and will be followed by a second report dealing with scale-up work. Pulverization to a −400-mesh powder was accomplished by oxidation to U$_3$O$_8$ in air or oxygen, the latter at reduced pressure, followed by reduction to uranium dioxide with hydrogen or by thermal decomposition to uranium dioxide at 1200°C.

Air proved to be the superior oxidant because the presence of the inert nitrogen diluent provided good control of the reaction and prevented resintering of the powder. Hydrogen reduction, although complicated by water vapor as a reaction product, was recommended over thermal decomposition under high vacuum. Optimum conditions consisted of oxidation in air at 1 atm pressure and ~375°C, followed by reduction in flowing hydrogen at 1 atm pressure and ~650°C.

A report has also been issued on the removal of irradiated uranium dioxide fuel from Zircaloy cans by oxidation[56] (previously described in *Reactor Fuel Processing*, 2(2): 21 (April 1959)). The oxidation reaction of uranium dioxide to U$_3$O$_8$ accomplishes pellet and particle breakup by an increase in lattice dimension, and the oxidized sample falls from the cladding. Removal rate versus temperature curves have been plotted for both air flow and oxygen flow. Optimum removal rate was obtained at 620 ± 10°C with oxygen and at 560 ± 10°C with air as the flow gas. The removal rate with oxygen is more than twice the rate obtained with air flow. The removal rate was also lower for irradiated material whose burn-up was not given. The simplicity of apparatus and of the techniques involved provides promise that scale-up will not be difficult. A furnace for the remote decladding of uranium dioxide has been designed and constructed.[57]

Preparations are now being made for carrying out the processing-refabrication experiment on 5-lb quantities of unirradiated uranium dioxide by gaseous oxidation and reduction. Apparatus is also being assembled for a hot cave experiment to process irradiated uranium dioxide on a 100-g scale to determine the fission-product decontamination and equipment contamination problems and to compare the behavior of irradiated and unirradiated uranium dioxide. Work on pellet refabrication equipment has begun with the design of a remote capsule welder.

2. *Carbide Fuels*. Work has been initiated at Atomics International on processing carbide fuels.[52, 57, 58] Presumably, the objective, as with oxide fuels, is to pulverize chemically, using reagents and temperatures which provide some fission-product volatilization and produce high-surface-area particles amenable to other process steps and reconversion to the carbide. Preliminary work has involved conversion to nitrides and chlorides. The uranium chlorides may be completely volatilized.

Miscellaneous

1. *Symposium on High-temperature Technology*. Papers presented at the recent International Symposium on High-temperature Technology were collected together by the planners and issued as "advance papers."[59] Presumably, a final edition of these papers will be issued in the future. As the second of these symposia, the recent conference records the developments of the last three years in fields depending on high-temperature technology. The conference dealt with such subjects as production and measurement of high temperature, properties of high-temperature materials and new materials developments, pyrometallurgy, high-temperature reactions, and high-temperature problems encountered with rockets and missiles.

2. *Containment of Molten Plutonium and Its Alloys*. Preliminary experiments have been completed to determine the reactions between molten plutonium and six oxide refractories (MgO, CaO, CeO_2, ThO_2, La_2O_3, and Y_2O_3).[49] Reaction rates increased with temperature but were high with MgO, CaO, and CeO_2. Reaction rates were very low with ThO_2 and Y_2O_3 and fairly low with La_2O_3 up to $1525°C$. The high reaction rate with CeO_2 is probably due to reduction to Ce_2O_3.

3. *Properties of "Fissium" Alloys*. Hardness, density, and thermal-expansion behavior of a series of uranium—fission product element alloys ("fissium") have been determined as-cast and as influenced by heat-treatment.[60] In cast and gamma-quenched material, retention of the high-temperature gamma phase produces low hardness and low density. The decomposition of retained gamma phase at $500°C$ results in a large increase in hardness and marked contractions. The behaviors are dependent on alloy composition and prior thermal history.

4. *Materials Development*. Slip-cast tungsten crucibles with densities of 97 per cent of theoretical have been prepared employing a nonaqueous suspending agent.[61]

Liquid Metal Fuel Reactor
Processing

The basic Liquid Metal Fuel Reactor (LMFR) concept is the use of a liquid metal as the carrier (solvent or suspending liquid) for fuel and fertile material. Bismuth is used because of its low neutron cross section, low vapor pressure, comparatively low melting point, and satisfactory uranium solubility. Magnesium and/or zirconium may be added to the bismuth to aid wetting of slurries and to minimize corrosion mass-transfer problems. The moderator is graphite and can be used uncanned in direct contact with the fuel. In the primary system the fuel is heated from 750 to $1050°F$ within the reactor; it is pumped from the reactor through a heat exchanger where it transfers the heat to sodium and back to the reactor. Early studies at Brookhaven National Laboratory (BNL) were based on design of a two-region breeder reactor system consisting of a uranium solution as the core fuel and a thorium bismuthide slurry as the breeder blanket. The BNL metal—fused chloride fuel-purification system was based on this design. A fused-fluoride volatility process proposed by ANL was also considered for this system.[62] Subsequent economic evaluation of reactor designs have shown the attractiveness of oxide slurry systems, particularly those involving single-region reactors which could be operated for several years without fuel processing. After a suitable oxide-bismuth separation, existing aqueous processing methods are applicable in this case.[63, 64]

Results of a study at Armour Research Foundation on the solubility of uranium in bismuth with various concentrations of magnesium and zirconium additives have been reported. Zirconium lowers greatly the solubility of uranium in bismuth.[64] At Babcock & Wilcox emphasis has more recently been placed on developing oxide slurry. An important problem is the resistance of the slurry to reduction in the presence of magnesium and zirconium additives. Carbide slurries were investigated and found to be unstable.[64,65]

Volatile fission products are proposed to be continuously removed from the reactor. This is important because the major reactor poison is the gas Xe^{135}. A detailed discussion of the concentration and required removal rates for xenon and its precursor, iodine, has been reviewed.[65] For a 1 per cent reactor poisoning level and assuming no xenon adsorbed on or absorbed in the graphite, the concentrations of Xe^{135} and total xenon in the fuel are estimated to be about 1.5 and 13 ppb, respectively, for a typical commercial plant. Complete isotopic compositions of the volatile fission products and poison levels for different removal rates are presented. The effects of various degrees of volatilization of the iodine and bromine are also shown. Proposed types of degassers are discussed. Both xenon and iodine have strong tendencies to adsorb on unwetted surfaces and to penetrate graphite, the moderator material in the reactor core. Such immobilization of xenon in the core would present a problem from the standpoint of reactor poisoning. Experimental results are presented to show the extents to which both iodine and xenon adsorb on steel and graphite and penetrate graphite. It appears that the xenon problem is not so much one of removing it from the fuel in a desorber as it is in preventing it from collecting on graphite surfaces in the core.

In a summary of work at ANL on the basic steps of the fused-salt fluoride volatility process, applied to LMFR solution fuel, data on the extraction of uranium, magnesium, cerium, zirconium, and niobium from bismuth with a molten mixture of sodium fluoride and zirconium fluoride have been obtained.[66] Comparative rates of extraction were determined. The effects of high concentrations of magnesium and of hydrogen fluoride sparging on the extraction process have been investigated. Tracer studies have demonstrated that exchange occurs between zirconium dissolved in the bismuth and zirconium in the

fused salt. It is economically attractive in this process to minimize fused-salt consumption by allowing the fission products to build up in the salt to as high as 2000 ppm. However, since magnesium is the most active element present, it will be oxidized and extracted with the fission products. The salt composition in this case will be high in magnesium fluoride, with a probable increase in melting point with this composition change. This work on solution fuel processing is not being continued.

Homogeneous Reactor Processing

Homogeneous reactors have the advantage that side streams of fuel can be removed continuously and processed for removal of fission-product activity. The degree of purification required for the process need not be high. An operating reactor of this type is the aqueous Homogeneous Reactor Test (HRT) at Oak Ridge.

It was reported in the preceding Review[1] that a multiple hydroclone assembly had been installed in the chemical processing pilot plant. The hydroclones are the primary separation device for the removal of accumulated solid corrosion and fission products. The modification increases the fuel processing rate from 1.8 to 10 gal/min. This was considered necessary because of the competing mechanism by which solids were being removed from the system — deposition on equipment side walls. The underflow from the multiple assembly is fed to the original single hydroclone. In the first two runs in which this equipment was used, the predicted increase in removal rate of three to four times that of the single hydroclone was realized,[10] but, after the HRT had been operated for 500 hr with the new system, removal rates were only 60 per cent higher. The decrease of the removal factor with time was explained on the basis of decreased hydroclone efficiencies. The average particle size removed has decreased from 1 to 0.8 μ, and from previous work it is known that such decrease results in a 50 per cent reduction in efficiency.[16] Further improvement of the system is sought by cycling a portion of the single hydroclone underflow back into the feed stream. If with these modifications the solids-removal rates drop off to values as low as those previously obtained with the single unit, this method of solids removal will be discontinued.[10] The method considered useful as an alternate is the

periodic dissolution of the scale and crud in the reactor system. Chemicals tested include chromous sulfate and uranous sulfate. Both reagents are effective but corrosive. There is some concern as to whether the reactor material of construction, Zircaloy-2, is subject to hydrogen embrittlement with the chemicals indicated.

It is proposed to dissolve the solids collected with the hydroclones by alternate treatments with boiling 10.8M sulfuric acid and 4M sulfuric acid following removal of heavy water by distillation. The solubilized uranium will then be purified by either ion-exchange or solvent-extraction techniques. A possible disadvantage to these processing methods is the necessity to store the fuel through a long decay period prior to processing. A suggested alternate is to process short-cooled material by peroxide precipitation in the heavy-water environment. The method was tested recently on HRT fuel.[10] Uranium losses during these procedures did not exceed 0.1 per cent, and decontamination factors varied from 5 for gross beta counts to 86 for that of copper. This appears to be adequate in view of the continuous processing philosophy.

Studies are continuing on an electrolytic method for the removal of nickel, copper, and manganese contaminants of the fuel. In laboratory and small-scale runs, all three elements were removed to the extent of 99 per cent or better when an agitated mercury cathode was used. When solid cathodes such as stainless steel or nickel were substituted, the efficiency of copper removal remained the same, but nickel efficiencies were greatly reduced. During the electrolysis, a percentage of the uranium is reduced to the $+4$ state. The original valent state is restored by treatment with an oxygen-ozone mixture.[10,22,67]

The behavior of iodine has received considerable attention. The incentives to remove it from the HRT fuel solution are twofold: the biological hazard and the prevention of the poisoning of the recombiner catalyst. In power reactors, iodine removal on a 45-min processing cycle would effectively control xenon poisoning.[10] The behavior of iodine in this system is complicated by several factors: the effect of the presence of 50 g of dissolved silver from the iodine trap is not clear, and it is known that iodine does adsorb on precipitated corrosion and fission products. The valence state of the iodine is not significantly affected by radiation.

From the data observed in the operation of the reactor system, it appears that the solubility of the rare earths is even less than laboratory data would indicate. The solubility of neodymium[10] appears to be on the order of 5 ppm.

The charcoal absorbers installed in the system for xenon and krypton absorption have operated much better than expected. Flow rates up to five times design capacity have been accommodated successfully. Studies were made on the effect of carbon dioxide (from possible combustion of the absorber) dilution of carrier gas on the elution characteristics or holdup times of the charcoal bed for the xenon-krypton. The holdup for krypton was reduced by a factor of 50 per cent when carbon dioxide was used as the carrier gas.

A bibliography of publications on the absorption of krypton and xenon on activated carbon has appeared during the past quarter.[68] The bibliography includes listings of 100 unclassified publications from 1905 to the present.

A discussion of the corrosion problems associated with the chemical processing plant of the HRT appears under the heading Corrosion in this Section.

Plant Design, Instrumentation and Equipment Development

Instrumentation and Equipment

A strain-gauge weighing system for determining the quantity of fuel in a continuous dissolver is now being readied for use on a prototype dissolver.[69] The system has an accuracy of ± 0.25 per cent for loads from 40 to 200 lb at temperatures between 15 and 115°F. Tare weights (basket) up to 100 lb may be suppressed.

An ultrasonic continuous-level gauge developed by Acoustica Associates, Inc., is said to operate independently of fluid type, temperature, dielectric constant, density, or viscosity.[70] Transducers are attached to rods extending into the liquid. One rod is used to send an acoustical pulse which is received by the other rod. The delay between sending and receiving this pulse is proportional to the depth of the liquid.

Modified versions of the Model S $\frac{3}{4}$-hp Chempump are undergoing life tests under various conditions.[15] One Chempump with 100 per cent oversized custom-made bearings failed after

2700 hr of continuous service. Another Model S $3/4$-hp Chempump has been modified for slurry use. The shaft was flame-plated with alumina oxide, and the carbon bearings had flame-plated metal inserts. A total of 264 hr of service was accumulated in pumping waste calciner scrub solution containing alumina particles before the pump had to be dismantled. Wear was found to be moderate.

A device consisting of a differential transformer and an eddy-current coil used to indicate the internal porosity in cast fuel elements has been tested in a high-gamma field.[71] The above components were irradiated in a flux between 4.7×10^5 and 1.6×10^6 rads/hr. The electrical output of the components was periodically monitored during gamma irradiation to a total exposure of 1.24×10^9 rads. No changes in the shape of traces recorded were noted. It was concluded that the performance of this device was satisfactory for its anticipated use in the EBR-II Fuel Cycle Facility.

Plant Design and Operation

A conceptual design[69] for a processing facility has been prepared based on processing 1000 lb of irradiated fuel per day. The fuel alloy composition has been assumed to be 20 per cent total uranium and 80 per cent zirconium. The uranium had an assumed enrichment of 5 per cent U^{235} prior to irradiation to 10,000 Mwd/ton. In the irradiation process, 300 g of plutonium has been produced per 1000 lb of irradiated fuel alloy (this is equivalent to 3000 g of plutonium for each ton of uranium irradiated). The spent fuel as fed to the processing plant had an enrichment of 3 per cent U^{235}. Investigations indicate that the facility design incorporates sufficient flexibility to process highly enriched irradiated fuels at a rate of 4.5 kg of uranium per day. Plant design has been based on a direct maintenance philosophy, and as a result design emphasis is directed toward an elimination of minor trouble spots through careful selection of equipment, instrumentation, etc., and sparing of critical items.

In the main facility a storage canal for fuel elements separates the processing area, containing the concrete cells with process equipment, from the service area, containing offices, maintenance shop, personnel facilities, and the laboratory. Requirements for operating personnel total 124 employees, and an organization chart of the operating and supervisory personnel is presented.

The process is based on dissolution of the uranium-zirconium alloy as developed at ANL, solvent extraction by a modified Hanford Purex process cycle, and plutonium isolation by the ion-exchange system developed at ORNL.

Total capital investment costs and annual operating costs have been determined for the chemical processing facility. Every effort has been made to determine actual costs and to minimize the use of factors. The total capital investment including equipment and installation, site, taxes, and start-up costs is approximately $3,723,800. The operating costs, including source-fissionable material inventory, chemicals, utilities, labor, etc., have been determined for processing both slightly enriched (3 per cent U^{235}) and highly enriched (90.9 per cent U^{235}) fuel. The costs are $3,583,662 and $4,436,274, respectively. Using these figures, the costs for processing U^{235} are $4.63 per gram of U^{235} fed for slightly enriched fuel and $3.94 per gram of U^{235} fed for highly enriched fuel.

Corrosion

Newly developed fuels, particularly those for power reactor purposes, require new methods of processing for recovery of the constituents, or at least modifications or additions to existing processing plants. New corrosion problems arise with each proposal. A systematic effort is made here to bring the reader up to date in those areas of chemical processing where specific corrosion programs have been established.

Solvent Extraction

The plants presently used for processing nuclear fuels are of the solvent-extraction type. Since many of the newer fuels cannot be dissolved by existing procedures, several AEC sites are developing head-end treatment procedures for such fuels that are compatible with the solvent-extraction plants. Corrosion and materials-of-construction problems arising from these efforts are described below.

Fuels of the type to be used in the Consolidated Edison reactor consist of a stainless-steel cladding over a core of thorium dioxide—uranium dioxide. Possible combinations of head-end treatments for these fuels include the so-called Sulfex-Thorex and Darex-Thorex processes.

These differ only in the decladding operation. In the Sulfex-Thorex process, the stainless-steel jacket is dissolved in boiling $6M$ sulfuric acid, whereas, in the Darex-Thorex process, this is accomplished with a mixture of $5M$ hydrochloric acid–$2M$ nitric acid. The core dissolution is accomplished in a nitric acid solution containing some fluoride ion. Scouting tests early eliminated all construction materials for these two processes except Nionel for the Sulfex-Thorex process and titanium for the Darex-Thorex process.

Further tests were made with Nionel and titanium to determine possible limitations. A status report has recently appeared.[72] In the corrosion of Nionel in the Sulfex decladding step, the zone of maximum attack is the interface region. In pure boiling $6M$ sulfuric acid, the corrosion at the interface is about 5 mils/month. As the decladding of the stainless-steel fuel continues, the accumulation of this dissolved cladding (iron, nickel, and chromium) up to about 35 g/liter results in decreased interface corrosion to 0.3 mil/month. In the core dissolution step, it was found that welded and heat-treated Nionel was sensitive to a form of intergranular attack when exposed to boiling initial Thorex solutions ($13M$ nitric acid, $0.04M$ fluoride, $0.2M$ aluminum) containing hexavalent chromium. This attack in some instances was found to be as high as 18 mils/month. With the chromium in the trivalent state, the rate was halved. It appears, however, that, when the two steps of the process are combined into a cycling exposure, any such intergranular or accelerating effects are either minimized or eliminated. Typical liquid-phase rates are about 2 mils/month. However, where welds have been poor, attack rates of up to 50 mils/month have been observed.[5,73] The presence of aluminum ions in the environment is essential to maintaining adequate corrosion control. Figure 6 shows the corrosion of Nionel (and titanium) in initial Thorex solutions as a function of aluminum concentration. It will be noted that the corrosion is improved by a factor of 20 by incorporating aluminum ($0.2M$) into the environment.

Titanium corrodes in boiling $2M$ hydrochloric acid–$5M$ nitric acid at an acceptable rate of less than 1 mil/month. Again, the accumulation of dissolved cladding in the solution serves to decrease the corrosion rate; 0.1 mil/month is typical. The corrosion of titanium in the core dissolution step is nearly as sensitive to fluo-
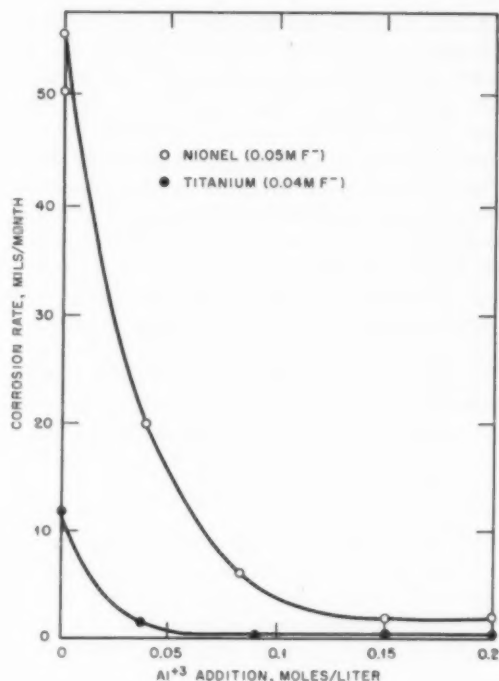

Figure 6—Maximum corrosion rates of Nionel and titanium in boiling nitric acid–sodium fluoride solutions with various Al^{+3} additions (24-hr exposures).[5,73]

ride ion as is Nionel. Additions of Al^{+3} ion to the extent of $0.05M$ reduced the corrosion rate in boiling Thorex solutions from 10 mils/month to 1 mil/month (see Fig. 6). The accumulation of thorium ion as the dissolution proceeds further decreases the corrosive attack. The combination of these factors results in an acceptably low corrosion rate in the cycled environment. Penetrations in a bench-scale dissolver were found to be less than 0.2 mil/month. A possible problem may exist in the vapor phase. With no aluminum in Thorex solutions, the vapor-phase attack is on the order of 8 mils/month. This is reduced by a factor of 4 where aluminum additions of $0.04M$ are made. However, when aluminum-ion concentration exceeds $0.04M$, some pitting tendencies have been observed.[4,6] Other possible problems have been anticipated. Chloride contamination of the second step could occur by virtue of insufficient rinsing following step one. Contamination of beginning Thorex solutions (with no Al^{+3}) with 100 ppm of chloride ion results in the corrosion of titanium at a rate of 8.3 mils/month, but this rate drops to

0.4 mil/month when the thorium concentration reaches 0.5M (references 4, 5, 18, and 73). More serious was the pitting which accompanied the attack. When beginning Thorex solutions were contaminated with 0.1M to 0.2M ferric ions, corrosion increased[3] to about 10 mils/month. Barring some rather unusual complications, it appears that titanium could be a very useful material of construction for the Darex-Thorex environment.

At Hanford the question has been raised as to whether the process wastes from a Sulfex process can be handled safely in the existing steel storage tanks. In subsequent corrosion tests, it was learned that small concentrations of ferric ion would reduce the corrosion to acceptable levels.[17,74] Concentrations on the order of 0.001 to 0.004 were adequate. Ferrous ions in the same concentrations were not effective. However, oxidation with 0.001M sodium dichromate reduced attack to acceptable values. Air sparging of Sulfex process wastes to oxidize ferrous ion to ferric ion may be adequate to make them compatible with the 304L stainless-steel storage vessel.[74]

Several new fuels consist of a core of uranium-molybdenum alloy clad with either aluminum or Zircaloy. Proposals for dissolution of the core alloy include the use of a nitric acid–ferric nitrate mixture. In scouting experiments for a construction material, stainless-steel type 304L and Hastelloy-F were found to be reasonably resistant. It is known, however, that excessively high concentrations of ferric nitrate result in intergranular attack. Threshold values of ferric nitrate concentrations were recently determined. These were found to be 0.6M for stainless-steel type 304L and 0.8M for Hastelloy-F. Following the dissolution of such fuel, a dichromate oxidation has been proposed as a feed-adjustment step prior to introduction in the solvent-extraction columns. At a nitric acid concentration level of 0.04M, the attack on stainless-steel type 304L is slight (less than 1 mil/month) and nonpreferential, whereas at higher concentrations (0.5M to 1.0M) the corrosion increased to 5 mils/month; some intergranular attack was also observed.[14,74]

In conjunction with the processing of the above fuel, it was learned at Brookhaven that additions of chromium to the dissolver solution would solubilize the precipitates formed. Chromium is known to accelerate the corrosion of the 300-series stainless steels in some oxidizing en-

vironments. Concern was indicated over the possible effect of the chromium additions in the waste evaporator which contains both 304L and 309 SCb stainless steel. Corrosion tests were made in which the reference environment was a boiling simulated waste of 6M nitric acid which had been saturated with tributyl phosphate. Increasing the chromium content from 0.01M to 0.06M resulted in corrosion increases from 30 to 230 mils/year for type 309 SCb stainless steel and 19 to 315 mils/year for type 304L.[75]

A type 347 stainless-steel dissolver used to investigate the processing of Enrico Fermi Reactor fuel was subjected to visual examination. Severe preferential weld-metal corrosion was observed. Total exposure time[75] to dissolution conditions was estimated at 300 hr.

The Zirflex process is applicable to decladding of zirconium- or Zircaloy-clad fuels. Where core materials consist of uranium dioxide, the core will be dissolved in 10M nitric acid containing small amounts of fluoride (0.05M). The results of scouting tests in the individual environments were reported in the preceding Review.[1] Haynes-21 alloy was found to be the most promising with type 309 Cb stainless steel and Nionel being runner-ups.[10] It has been determined more recently that additions of 0.05M B_4O_7 (and 0.05M SiO_3) decrease the corrosion of welded and heat-treated Nionel in the decladding environment from 8 to 6 mils/month.[72,73] Results of cyclical exposures were also reported (the cycles were not defined but are presumed to coincide with the above-listed environments). Type 309 SCb stainless steel and Nionel were found to have corrosion rates of less than 2 mils/month after 8 to 10 of the cyclical exposures (references 3 to 5, 18, and 73). However, in one test where welded 309 SCb was used, some cracking and pitting were observed.[4]

At the Savannah River laboratories consideration is being given to Enrico Fermi Reactor fuel consisting of a core of 10 per cent molybdenum–90 per cent uranium clad with Zircaloy. One proposal is to dissolve the cladding in 0.07M hydrofluoric acid followed by dissolution of the core alloy by adding nitric acid containing aluminum nitrate. From present results, it appears that the existing dissolver made of type 309 SCb stainless steel would be compatible with this process.[76] This proposal bypasses a serious corrosion problem that existed in earlier proposals which involved the use of 0.075M hydrofluoric acid–3.0M nitric acid. Measured

attack rates of arc welds made of 309 SCb stain-
less steel were on the order of 630 mils/year
compared to 25 for unwelded material. In boiling
hydrofluoric acid (the new proposed decladding
environment), the corrosion rates of the wrought
and welded stainless steel are about comparable
(40 mils/year). In the core dissolution step the
addition of aluminum to complex fluoride is es-
sential. Figure 7 shows the effect of "free fluo-
ride" on the corrosion of type 309 SCb stainless
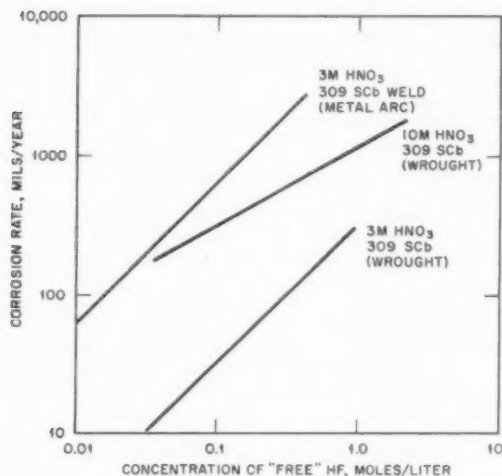steel as determined at the Savannah River
laboratories.[76]

Figure 7 — Effect of "free fluoride" on corrosion of
309 SCb weld and wrought metal.[76]

Corrosion information on the so-called Per-
flex process has been appearing in recent re-
ports (references 3 to 6, 18, and 73). The refer-
ence environment used in tests is boiling $1M$
hydrofluoric acid—$0.06M$ hydrogen peroxide.
Materials having corrosion rates in excess of
14 mils/month include Nionel, Carpenter-20,
Haynes-25, and pretreated Monel. Hastelloy-C,
the most recently tested alloy, appears to be the
most promising, having corrosion rates on the
order of 5 mils/month.[18, 73]

Construction materials for the storage of
solvent-extraction processing wastes continue
to be of interest. The acidic Purex first-cycle
waste is currently receiving attention. Corro-
sion tests made in this environment containing
$6M$ nitric acid and $0.8M$ to $1.6M$ sulfuric acid
indicate that stainless steels 304L, 316L, and
309L have reasonable rates of dimensional

change (1 to 3 mils/month). However, all ap-
pear to be subject to intergranular attack, with
the first two alloys being more sensitive than
the 309L (the exposures were at the boiling
point).[28] E-55 titanium subjected to the same
environment had no subsurface attack, and di-
mensional change was on the order of 0.2 mil/
month maximum. Additional tests were made in
which the acidic Purex waste was concentrated
to 60 per cent of the original volume, and the
nitric acid was destroyed by formaldehyde. The
same alloys plus zirconium and Nionel were then
exposed at the boiling point to the solution. The
stainless steels and Nionel were again subjected
to intergranular attack, and zirconium was found
to have a dimensional change rate of less than
0.01 mil/month.[54]

A proposal to modify the Zircex process to
improve uranium recovery has the incidental
benefit of reducing construction-material prob-
lems.[10] The original process consisted of hy-
drochlorinating zirconium fuels at 500°C with
anhydrous hydrochloric acid, followed by the
dissolution of uranium trichloride residues in
nitric acid. The difficulty was to find a con-
struction material which was compatible with
both the hydrochlorination step and the nitric
acid dissolution step. In the newly proposed flow
sheet an additional step is inserted between the
two existing ones. This consists in the chlori-
nation with carbon tetrachloride of the uranium
trichloride residue together with some residual
zirconium. The resulting volatile chlorides are
condensed in a second vessel, where dissolution
of the sublimate is accomplished with nitric
acid. In this procedure Inconel can be used for
the first process vessel and titanium for the
second. Each is compatible with the process
step being conducted.[10]

Aqueous Homogeneous Reactor Processing

The results of an extensive corrosion testing
program on the environments encountered in the
chemical processing plant at the HRT at Oak
Ridge have been reported.[77] The solid corro-
sion and fission products in the HRT are re-
moved continuously with the use of hydroclones.
These solids, together with some fuel solution,
are periodically removed from the collection
vessel below the hydroclone and are discharged
to a dissolving system. Following the removal
of heavy water by evaporation, the residual
solids are sulfonated in boiling $10.8M$ sulfuric

acid and solubilized by diluting to $4M$ acid. The cycle is repeated until complete dissolution has occurred. The resulting solution is transferred to storage vessels for decay prior to processing in solvent-extraction plants. Three reference environments were selected for the corrosion testing program: (1) boiling $10.8M$ sulfuric acid, (2) boiling $4M$ acid, and (3) $4M$ acid at $38°C$. Additional parameters tested included the effect of additions of synthetic corrosion and fission products and the effect of oxygen, helium, or no aeration. In two tests the effect of ruthenium additions to boiling $4M$ sulfuric acid was also examined. A tabulation of the data obtained is shown in Table III-5.

results were negative. The selection of a material for the storage vessels and pipe lines associated therewith is less obvious. The concern exhibited is that process design conditions may not at all times be maintained. Inadvertent rises in temperature may be expected. At the extreme, the boiling condition, Carpenter-20 Cb exhibits the lowest rate of attack; however, it is susceptible to stress-corrosion cracking. The latter is inhibited by the presence of corrosion and fission products. The alternate materials are the 300-series stainless steels which have low corrosion rates at the boiling point, provided that corrosion and fission products are present. However, in the absence of the latter,

Table III-5 SUMMARY OF CORROSION DATA FOR HRT CHEMICAL PROCESSING PLANT[77]

| | Corrosion rate, mils/year | | | | | | | | | |
| | Boiling $10.8M$ H_2SO_4 | | | $4M$ H_2SO_4 at $38°C$ | | Boiling $4M$ H_2SO_4 | | | | |
	No aeration	Oxygen aeration	Oxygen and additives	Helium aeration	Oxygen and additives	Helium aeration	Oxygen aeration	Helium and additives	Oxygen and additives	He plus Ru
Aluminum oxide				Gain	Gain	10	6	6	10	
Carpenter-20 Cb S.S.	39,000	22,000	270	<1	<1	32*	3	2	2	172
Graphitar 14						Gain	Gain	Gain	Gain	
Hastelloy-B	43	24	320	<1		3	725†	>15,000	>15,000	41
Hastelloy-C							215		475‡	
Illium-R	10,000	1,150		<1	<1	15†	78‡	30†	30	
Chemical lead	34	108	31	<1		<1	3	1	3	
Stellite 6				12		43,000	25,000†	15†‡	20	
Stellite 98M2						5,900	2,400†	135†‡	240	
Tantalum	<1	<1	<1	<1	<1	<1	<1	<1	<1	
309 SCb S.S.					<1			2		
316 S.S.				8	<1	76,000	79,000	4	5	
347 S.S.					<1	89,000	118,000	4	8§	
Zircaloy-2	11	5	680	<1	<1	<1	<1	<1	<1	
Zirconium,							<1			
crystal bar	6	8	200	<1	<1	<1	<1	<1	<1	

*Cracked.
†Selective grain attack.
‡Pitting attack.
§End grain attack.

On the basis of the results shown, the selection of tantalum for the dissolution step of the process is reasonably obvious. Zircaloy-2 and zirconium crystal bar, although having reasonably low rates in clean boiling-acid solutions, exhibit an acceleration of attack with the addition of corrosion products and fission products which is not acceptable. Selected specimens of tantalum were analyzed by the vacuum-fusion technique for hydrogen to determine whether it was susceptible to hydrogen embrittlement. The

corrosion rates become catastrophic. The conservative approach in anticipating the worst conditions dictates the selection of Carpenter-20 Cb as the compromise material.

Fluoride Volatility Corrosion

In the fused-salt volatility process, zirconium matrix fuels are dissolved in a molten fluoride medium through which anhydrous fluoride is passed. Fluorine is passed through the homoge-

neous melt following the dissolution. The uranium, along with some fission products, is volatilized, condensed, and finally purified by distillation techniques or by adsorption on sodium fluoride traps. Where molten salt is used directly as fuel, only the second step need be used to recover and purify the uranium values.

The second nickel pilot-plant fluorinator at ORNL has been dismantled and is in the process of being examined and evaluated by Battelle Memorial Institute for corrosion effects.[78-80] The areas of the vessel that were most seriously attacked included the molten-salt phase and the liquid-vapor interface. Dimensional changes of up to 83 mils were observed in the liquid phase, and intergranular attack in comparable regions ranged up to 33 mils. Some evidence exists that sulfur may be responsible for the intergranular attack, although the possibility that it is due to fluorine is not being overlooked. By far the greatest dimensional attack occurred during the portions of the process in which fluorine was passed through the melt. The exposure to molten salt in the absence of fluorine was a small contribution. The total exposure time to molten salt was determined as 1940 hr, in which the sparge volume of fluorine was 60,000 liters.

Battelle is also examining portions of a small hydrofluorinator unit constructed of INOR-8. Substantial intergranular penetration was found in the vicinity of the interface and the region somewhat above. No intergranular attack or pitting was observed in the liquid phase. Because of large corrosion rates, the decision has been made to lower the dissolution temperatures.[10]

A rather basic study is being conducted at ANL on the reactions of fluorine with various metals, both construction and process materials. These include nickel and nickel alloys, uranium, and zirconium. Some preliminary results have been made available on reaction rates with nickel.[80] In studies made at 500, 600, and 700°C, it appears that the differences in surface pretreatment — acid dipped versus polished — are relatively small. This was true at varying exposure times up to 5 hr. It has been noted, however, that differences between L nickel and A nickel do exist. It appears that, at all temperatures, L nickel has the lower reaction rate, with the difference being small at 500°C and increasing to a 12-fold factor at 700°C (5-hr exposure).

In another study at the Oak Ridge Gaseous Diffusion Plant involving the corrosion char-

acteristics of nickel and nickel alloys in high-temperature fluorine environments, the temperatures[81] studied have gone up to 982°C. At 1300°F (704°C) the corrosion rate of Monel was about 40 times that of nickel. The pressure dependence of the uptake of fluorine on nickel was first order at both 1100 (593°C) and 1300°F. At 1500°F (816°C) the fluorine uptake was less pressure dependent. Furthermore, the rates of uptake at 1300 and 1500°F were comparable. The hypothesis presented for this phenomenon is that, at 1300°F, the metal was being subjected to an annealing process in which the nickel atoms along grain boundaries were particularly mobile. At 1500°F it is presumed that the annealing process was complete and, hence, that the mobility of the nickel atoms was lower. The subsequent migration of nickel to the surface and through the fluoride film constitutes the remaining portion of the mechanism.

The fluoride films were found to be reasonably adherent on nickel up to temperatures of 1800°F (982°C). Examination with the electron microscope revealed that these films were polycrystalline in nature and were, in general, one crystal layer thick. It was observed that greater resistance to the fluorine developed with the increasing film thickness.[81]

LMFR Fuel Processing

A fused-salt extraction process for bismuth-uranium fuels uses a ternary eutectic of sodium chloride, potassium chloride, and magnesium chloride to which an oxidant (bismuth chloride) is added. The construction materials contemplated for use in the existing process appear to be reasonably well in hand with the exception of the environments that include 5 per cent bismuth chloride. Molybdenum has appeared to be the most promising. In recent tests in this environment, gold was tested for 1000 hr in each of two tests and corrosion was found to be very low.[82] The exposure temperature was 500°C on the hot end and 450°C on the cold end. The test was of the rocking-furnace type. It was observed that none of the bismuth chloride was reduced by the gold.

Waste Processing

Two sets of corrosion evaluations were made on the calcination of an aqueous solution of $0.54 M$ zirconium fluoride and $0.75 M$ aluminum nitrate. In the first set of experiments, two

steps were used. The material was first cal-
cined in a rotary ball kiln at 300°C to decompose
the nitrates. A second kiln was used at 700°C
to convert the zirconium fluoride to oxide. In
the second set of experiments, a single kiln was
operated at 700°C to perform both the denitra-
tion and defluorination functions.[83] Corrosion-
wise it was found that there was no particular
advantage in operating the system as a two-
kiln procedure. Corrosion rates were higher,
and the equipment was more complicated. The
authors concluded that Illium-G, Inconel-X,
Haynes-25, and Nionel were the most suitable
materials; all corroded at rates of less than 15
mils/year.

An interesting technique was used to deter-
mine the corrosion rate. A sleeve and a core
were very accurately machined with a tolerance
of 0.1 mil. The core was inserted into the sleeve
by submerging the core in liquid air and heating
the sleeve. Following the exposure, a cross sec-
tion was made and the area of the core was de-
termined with a planimeter on a photographic
print, thus establishing the magnification. Then,
again using the planimeter, the area of the sleeve
was determined, and from this the corrosion
was determined.[83]

Pyrometallurgical Processing

Pyrometallurgical methods have value in that
the processing is accomplished without changing
the phase of the fuel. Techniques utilized include
oxide slagging, molten-metal extraction, crys-
tallization, and filtration. The corrosion in-
vestigations of construction materials for molten
plutonium are of interest to this work. It had
been learned earlier that the behavior of tanta-
lum in molten plutonium-iron eutectic alloy
varied considerably from test to test. When the
plutonium-iron alloy was made from cast iron,
the resistance of tantalum appeared to be good.
This was traced directly to the carbon content.
In most recent tests plutonium-iron alloy made
from cast iron showed no tantalum-transfer
characteristics during exposures[61] of up to 350
hr at 700°C. High-purity fuel showed mass-
transfer rates of approximately 30 mils/year.
High-purity fuel with additions of silicon and
manganese corroded at rates of 10 mils/year.
High-purity tantalum thimbles were tested at
650°C at exposure times of 500, 1500, 2500, and
4000 hr. No intergranular attack was found in

any of these tests, and general solution attack
was negligible, if present at all.[84]

At ANL, corrosion testing in pyrometallurgi-
cal processing environments has continued.[30]
The decision has been made that, in view of the
difficulties associated with the containment of
molten zinc, all future flow sheets will be based
on cadmium-base solutions. In static tests com-
pleted prior to the decision, molten zinc at
750°C was found to corrode the following metals
seriously: nitrided and cyanided steels, Therme-
nol, Haynes-25, Multimet, and Haynes Stellite
6B. Additions of 46 wt.% magnesium to the zinc
appear to reduce the attack substantially. In
dynamic tests capsules were loaded into a
stainless-steel box which was rotated in a
furnace at approximately 20 rpm. A series of
tests was made in this apparatus at 550°C for
963 hr in four cadmium-base environments as
follows: (1) no alloy additions, (2) 2 per cent
uranium, (3) 5 per cent magnesium, and (4) 8
per cent zinc and 2 per cent magnesium. No
dimensional change or intergranular attack
was observed in the cadmium or cadmium-
magnesium environment. Some interaction with
uranium in the second environment was found,
and intergranular corrosion to a depth of less
than 0.1 mil was observed in the fourth environ-
ment.[30] A liquid-metal circulating loop was de-
signed, constructed, and started up to investi-
gate more extensively the dynamic corrosion
characteristics of liquid-metal environments.
The construction material for this loop is mild
steel. The first environment to be investi-
gated is 2 wt.% uranium – 0.2 wt.% magnesium-
cadmium alloy. The operating temperature[30] is
550°C.

References

1. *Reactor Fuel Processing*, 2(4): (October 1959).
2. Oak Ridge National Laboratory, June 1959. (Un-
   published.)
3. Oak Ridge National Laboratory, September 1959.
   (Unpublished.)
4. Oak Ridge National Laboratory, July 1959. (Un-
   published.)
5. Oak Ridge National Laboratory, July 1959. (Un-
   published.)
6. Oak Ridge National Laboratory, May 1959. (Un-
   published.)
7. K. A. Allen and W. J. McDowell, Emulsion Stabi-
   lization by Silicic Acid, ORNL-2771, Aug. 31,
   1959. (Unclassified AEC report.)

8. K. B. Brown et al., Chemical Technology Division, Chemical Development Section C, Monthly Progress Report for August 1959, CF-59-8-45, 1959. (Unclassified AEC report.)

9. D. J. Crouse and K. B. Brown, Recovery of Thorium, Uranium, and Rare Earths from Monazite Sulfate Liquors by the Amine Extraction (Amex) Process, ORNL-2720, Aug. 3, 1959. (Unclassified AEC report.)

10. Oak Ridge National Laboratory, September 1959. (Unpublished.)

11. K. B. Brown et al., Chemical Technology Division, Chemical Development Section C, Monthly Progress Report for July 1959, CF-59-7-68, 1959. (Unclassified AEC report.)

12. Oak Ridge National Laboratory, September 1959. (Unpublished.)

13. U. Bertocci, Some Observations on the Extraction of Nitric Acid, Uranium, and Plutonium by Tri-Isononylamine, AERE-R-2933, May 1959. (Unclassified British report.)

14. L. P. Bupp, Hanford Atomic Products Operation, July 10, 1959. (Unpublished.)

15. C. E. Stevenson, Idaho Chemical Processing Plant Technical Progress Report for October Through December 1958, IDO-14467, May 19, 1959. (Unclassified AEC report.)

16. W. Davis, Jr., Radiation Densities and TBP Radiolysis During Thorex Short Decay Runs, ORNL-2764, Aug. 20, 1959. (Secret AEC report.)

17. L. P. Bupp, Hanford Atomic Products Operation, Aug. 10, 1959. (Unpublished.)

18. Oak Ridge National Laboratory, August 1959. (Unpublished.)

19. S. H. Jury and M. E. Whatley, Equilibrium Calculations in the System: Uranyl Nitrate, Nitric Acid, Water, TBP, and Kerosene Diluent Using the Oracle Digital Computer, CF-59-8-122, Aug. 12, 1959. (Unclassified AEC report.)

20. *Reactor Fuel Processing*, 2(3): (July 1959).

21. *Reactor Fuel Processing*, 2(2): (April 1959).

22. Oak Ridge National Laboratory, Sept. 4, 1959. (Unpublished.)

23. S. H. Jury and J. B. Adams, Uranyl Sulfate-Dowex 21K Anion Exchange: A Literature Survey, Review of Preliminary Data and Outline of a Proposed Experimental Program, CF-59-5-127, May 14, 1959. (Unclassified AEC report.)

24. J. L. Ryan, Concentration and Final Purification of Neptunium by Anion Exchange, HW-59193, Feb. 10, 1959. (Unclassified AEC report.)

25. J. K. Foreman, I. R. McGowan, and T. D. Smith, Some Aspects of the Anion-Exchange Behavior of Uranyl Nitrate in the Presence of Other Organic Nitrides, *Journal of the Chemical Society*, 738 (February 1959).

26. H. Pollock and R. M. Wallace, Behavior and Identification of Extractable Ruthenium, DP-344, March 1959. (Confidential AEC report.)

27. C. B. Amphlett et al., The Separation of Rubidium and Phosphorus on Zirconium Phosphate, *Journal of Inorganic & Nuclear Chemistry*, 10: 69-73 (1959).

28. L. P. Bupp, Hanford Atomic Products Operation, Sept. 10, 1959. (Unpublished.)

29. M. B. Goren, A Recovery Scheme for Poisoned Ion-exchange Resins, *Industrial and Engineering Chemistry*, 51: 539-542 (1959).

30. S. Lawroski et al., Chemical Engineering Division Summary Report, April, May, June, 1959, ANL-6029, September 1959. (Unclassified AEC report.)

31. D. O. Campbell and G. I. Cathers, Processing of Molten Salt Power Reactor Fuel, ORNL-CF-59-2-61, Apr. 1, 1959. (Unclassified AEC report.)

32. I. E. Knudsen, N. M. Levitz, and S. Lawroski, Preliminary Report on Conversion of Uranium Hexafluoride to Uranium Dioxide in a One-Step Fluid-Bed Process, ANL-6023, August 1959. (Unclassified AEC report.)

33. V. Y. Labaton and K. D. B. Johnson, The Fluorides of Uranium-III. Kinetic Studies of the Fluorination of Uranium Tetrafluoride by Fluorine, *Journal of Inorganic & Nuclear Chemistry*, 10: 74-85 (1959).

34. V. Y. Labaton, The Fluorides of Uranium-IV. Kinetic Studies of the Fluorination of Uranium Tetrafluoride by Chlorine Trifluoride, *Journal of Inorganic & Nuclear Chemistry*, 10: 86-93 (1959).

35. R. C. Liimataäinen, Vapor-Liquid Equilibrium of the System Bromine Pentafluoride—Uranium Hexafluoride, ANL-6003, May 1959. (Unclassified AEC report.)

36. G. A. Rampy, The Reaction of Uranium Dioxide with Uranium Hexafluoride, GAT-265, June 5, 1959. (Unclassified AEC report.)

37. J. Dykstra and W. C. Paris, The Use of Karbate Anodes in Fluorine Cells, K-1428, August 1959. (Unclassified AEC report.)

38. H. S. Brown and E. G. Bohlmann, Recovery of Plutonium from Cerium Trifluoride by Fluorination, U. S. Patent 2,873,168, Feb. 10, 1959.

39. H. S. Brown and D. W. Webster, Recovery of Plutonium Values by Fluorination and Fractionation, U. S. Patent 2,869,982, Jan. 20, 1959.

40. F. H. Spedding and A. S. Newton, Volatile Fluoride Process for Separating Plutonium from Other Materials, U. S. Patent 2,882,125, Apr. 14, 1959.

41. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., Vol. 6, No. 9, September 1959.

42. F. H. Spedding, T. A. Butler, and I. B. Johns, U. S. Patent 2,877,109, March 1959.

43. Argonne National Laboratory, September 1959. (Unpublished.)

44. Chemical Engineering Division Summary Reports for the Period April 1957 to July 1959: ANL-5759, -5789(Del.), -5924, -5959, -5996, and -6029, Unclassified AEC reports; ANL-5820, -5858, and

-5896, Confidential AEC reports; ANL-6068, Unpublished.

45. K. R. Ferguson and L. M. Safranski, in Sixth Hot Laboratories and Equipment Conference, March 19-21, 1958, TID-7556, pp. 160-167, April 1959. (Unclassified AEC report.)

46. Donald J. Stoker, An Elevating Turntable for Remote Maintenance in the Processing-Refabrication Experiment, NAA-SR-3264, Aug. 15, 1959. (Unclassified AEC report.)

47. Annual Report on Fundamental Research and Development in Metallurgy for July 1957 to June 1958, NMI-1215, Sept. 1, 1959. (Unclassified AEC report.)

48. Monthly Newsletter from Ames Laboratory, A. F. Voigt to J. Simmons, July 1959. (Unclassified.)

49. U. S. Atomic Energy Commission, January 1959. (Unpublished.)

50. Monthly Newsletter from Ames Laboratory, A. F. Voigt to J. Simmons, August 1959. (Unclassified.)

51. H. T. Hahn and E. M. Vander Wall, Salt-Phase Chlorination of Reactor Fuels. I. Dissolution of Zirconium Alloys in Lead Chloride, IDO-14478, May 22, 1959. (Unclassified AEC report.)

52. Atomics International, Chemical Processing Development Newsletter for July 1959. (Unclassified.)

53. C. T. Brown et al., Bibliography on Molten Salts, Technical Note No. 9, AFOSR-TN-58-773, September 1958. (Unclassified USAF report.)

54. L. P. Bupp, Hanford Atomic Products Operation, October 1959. (Unpublished.)

55. S. Strausberg and T. E. Luebben, Chemical Pulverization of Sintered Uranium Dioxide Bodies. Part I. Preliminary Small-scale Studies, NAA-SR-3910, Aug. 1, 1959. (Unclassified AEC report.)

56. L. A. Hanson, Removal of Irradiated UO_2 Fuel from the Cladding by Controlled Oxidation, NAA-SR-3591, Aug. 1, 1959. (Unclassified AEC report.)

57. Atomics International, Chemical Process Development Newsletter for August 1959. (Unclassified.)

58. Atomics International Newsletters for June, July, and August 1959. (Unclassified.)

59. Stanford Research Institute, Advance Papers of an International Symposium on High-temperature Technology, October 6-9, 1959.

60. S. T. Zegler and M. V. Nevitt, *Nuclear Science and Engineering*, 6: 222-228 (September 1959).

61. U. S. Atomic Energy Commission, February 1959. (Unpublished.)

62. *Reactor Fuel Processing*, 1(3): (July 1958).

63. Report of the Fluid Fuel Reactors Task Force, TID-8507, February 1959. (Unclassified AEC report.)

64. Liquid Metal Fuel Reactor Experiment Annual Technical Report, BAW-1136, Mar. 25, 1959. (Unclassified AEC report.)

65. O. E. Dwyer and A. M. Eshaya, On the Removal of Volatile Fission Products from Uranium-Bismuth Reactor Fuels, *Nuclear Science and Engineering*, 6(4): 350 (October 1959).

66. Max D. Adams et al., Extraction of Uranium, Magnesium, and Cerium from Bismuth with a Fused Fluoride Salt Mixture, ANL-6017, June 1959. (Unclassified AEC report.)

67. J. C. Bresee et al., Oak Ridge National Laboratory, July 1959. (Unpublished.)

68. L. A. Weller, The Adsorption of Krypton and Xenon on Activated Carbon — A Bibliography, MLM-1092, May 6, 1959. (Unclassified AEC report.)

69. V. R. Cooper, Quarterly Report, Technology of Non-Production Reactor Fuels Reprocessing, HW-59891, July 2, 1959. (Unclassified AEC report.)

70. Ultrasonic Instruments for Level, Flow, and Pressure, *Automatic Control*, 11: 22 (September 1959).

71. G. J. Pokorny and J. E. Ayer, The Performance of a Special Differential Transformer and an Eddy Current Coil in a High Gamma Flux Environment, ANL-5988, July 1959. (Unclassified AEC report.)

72. W. E. Clark, Oak Ridge National Laboratory, June 1959. (Unpublished.)

73. Oak Ridge National Laboratory, August 1959. (Unpublished.)

74. V. R. Cooper, Quarterly Report, Technology of Non-Production Reactor Fuels Reprocessing, HW-62063, Sept. 24, 1959. (Unclassified AEC report.)

75. C. W. Pierce, Reprocessing of Power Reactor Fuels, The Enrico Fermi Fast Breeder Reactor Fuel Progress Report No. 2, BNL-549, March 1959. (Unclassified AEC report.)

76. E. S. Occhipinti, comp., Reprocessing of Power Reactor Fuels, Quarterly Progress Report No. 6 for January 1 to April 1, 1959, DP-393, June 1959. (Unclassified AEC report.)

77. J. L. English, J. C. Griess, and D. J. Krause, Corrosion Studies for the HRT Chemical Processing Plant, ORNL-2735, July 24, 1959. (Unclassified AEC report.)

78. R. W. Dayton and C. R. Tipton, Jr., Progress Relating to Civilian Applications During July 1959, BMI-1366, Aug. 1, 1959. (Confidential AEC report.)

79. R. W. Dayton and C. R. Tipton, Jr., Progress Relating to Civilian Applications During August 1959, BMI-1377, 1959. (Confidential AEC report.)

80. R. W. Dayton and C. R. Tipton, Jr., Progress Relating to Civilian Applications During September 1959, BMI-1381, 1959. (Confidential AEC report.)

81. C. F. Hale et al., Carbide and Carbon Chemicals Co., May 1959. (Unpublished.)

82. LMFR Bimonthly Progress Report for May-June 1959, Brookhaven National Laboratory.

83. E. J. Tuthill and R. F. Domish, Study of Corrosion on Various Metals in the Calcining of Aqueous Radioactive Wastes Containing Zirconium Fluoride and Aluminum Nitrate as Bulk Salts, BNL-510, May 1958. (Unclassified AEC report.)

84. U. S. Atomic Energy Commission, September 1959. (Unpublished.)

85. LMFR Bimonthly Progress Report for March–April 1959, Brookhaven National Laboratory.

Congressional Hearings

In a previous Review[1] reference was made to the Congressional hearings on waste disposal held by the Joint Congressional Committee on Atomic Energy in January and February 1959. Four volumes (3057 pages) of oral testimony and submitted papers are now available.[2] These volumes form an excellent reference source on most aspects of waste disposal. A Summary-Analysis of the hearings has also been published.[3]

On July 29, 1959, the Special Subcommittee on Radiation held an additional public hearing on the specific subject of disposal of low-level radioactive waste into the ocean. In particular, the meeting was called to receive testimony on the National Academy of Sciences – National Research Council (NAS-NRC) report entitled "Radioactive Waste Disposal into Atlantic and Gulf Coastal Waters." This report suggested 28 possible locations for disposal of low-level wastes in "in-shore areas," in some cases less than 15 miles from shore and in waters less than 50 fathoms (300 ft) deep.

The hearing also considered HR-8187 and HR-8423, bills introduced in July and referred to the Joint Committee, which would impose certain statutory restrictions on disposal of radioactive materials in the Gulf of Mexico or in the Atlantic Ocean.

During the hearings, representatives of the Atomic Energy Commission indicated that the AEC has not yet approved the locations suggested by the NAS-NRC report. The AEC stated that it would continue to follow a policy of disposing of radioactive wastes in depths of not less than 1000 fathoms which, in most cases, would mean sites at a distance from 70 to 150 miles offshore. The AEC further stated that it would not grant licenses for disposal in "in-shore areas" without first notifying the Governor of the contiguous state and providing opportunity for public hearings on the proposed license as required by the AEC rules of practice. The AEC assured the Joint Committee that the present policy of disposing of wastes in not less than

1000 fathoms would be continued until scientific evidence had clearly demonstrated after further studies and research that disposal in lesser depths and nearer to the shore could be made without injurious effects upon fisheries, man, and his environment.

Uranium Mill Effluents

Secretary Arthur S. Flemming of the U. S. Health, Education, and Welfare Department announced in July 1959 that an agreement had been reached with the Vanadium Corp. of America to prevent contamination of the Animas River in Colorado and New Mexico by radium from uranium milling operations in Durango, Colo.[4] A U. S. Public Health Service survey conducted in 1958 and 1959 indicated that the radioactive content of the river water ranged from 40 to 160 per cent above maximum permissible levels. The Vanadium Corp. has agreed to install facilities to remove all possible radium from its waste water, and the Public Health Service will conduct an evaluation of the remedial facilities later this year.

The AEC, in cooperation with the Public Health Service, is also conducting negotiations with a number of other mill operators relative to the discharge of radioactive effluents into adjacent streams and has declared that performance in accordance with submitted company plans to eliminate any excess radioactivity will be made a condition of AEC licensing. These plants include the Uravan, Colo., and Green River, Utah, mills of the Union Carbide Nuclear Co.; the Maybell, Colo., mill of Trace Elements Corp. (a unit of Union Carbide Corp.); the Salt Lake City, Utah, mill of the Vitro Uranium Co.; and the Moab, Utah, mill of Uranium Reduction Co.

A detailed report bearing on this problem[5] was issued during the quarter. Samples of tailing-pond water from various mills were analyzed for uranium, Th^{230}, Th^{234}, and Ra^{226}. Radium was the one isotope whose specification was always grossly exceeded. Uranium and Th^{230} were found to be in excess in certain individual

samples. Radium was found to be removed from acid tailings by two means. Simple neutralization removed radium by coprecipitation and adsorption on the precipitated material. Contact of the radium-bearing solution with natural barium sulfate, or barite, provided a specific process for removing radium by adsorption and, possibly, inclusion into the barite. The neutralization-barite treatment process was also shown to be effective in decontaminating alkaline tailings.

Reduction to Solids

The adsorption of activity onto clays, soil, and mica; its incorporation into glasses; and three methods of calcination are discussed.

Adsorption on Natural Materials

The adsorption of radioactive nuclides by Savannah River Plant soil was measured as a function of pH and cation concentration.[6] For all nuclides studied, the adsorption was inhibited by high concentrations of hydrogen ion. Maximum adsorption occurred between pH 7 and 9. The presence of high concentrations of sodium and aluminum ions inhibited the adsorption of both cesium and strontium.

The effect of pH on the adsorption of nuclides that are readily hydrolyzed (Pu, Zr-Nb) is complicated by the formation of hydrolytic species at a high pH. The adsorption of these nuclides by soil is generally favorable from neutral solutions. The presence of trace quantities of oxalate ion reduces the effectiveness of soil in adsorbing zirconium and niobium. The adsorption of ruthenium depends on hydrogen-ion concentration and the nature of the ruthenium species in solution. Maximum adsorption occurs from neutral solutions; however, a fraction of the ruthenium in these solutions does not adsorb under any conditions.

Eighty-three hundred column volumes of a synthetic waste simulated to contain 24 μc of Cs^{137} per liter were decontaminated by a factor greater than 500 by passage through a 50-g column of clinoptilolite at a flow rate of 2.8 gal/(sq ft)(min).[7] The adsorption of cerium by clinoptilolite is not significantly reduced by decreasing the pH from 12 to 1. Strontium decontamination drops sharply, however, as the pH is reduced below 3.

The structure of the mica crystal allows for considerable variability in its chemical composition, and it should be possible to incorporate fission products as well as corrosion products and other inactive material into mica without destroying its physical integrity. The possibility of using synthetic mica for this purpose is being studied in France,[8] and at the Johns Hopkins University similar work is being done using synthetic feldspar.[9] The preparation of mica, by heating feldspar with magnesium oxide and magnesium fluoride, and the production of solid pellets, by mixing the mica with glass frit and subjecting it to pressure and temperature, have been described.[10]

Synthetic fluor-phlogopite incorporating Cs^{137} was produced in a solid-state reaction by heating for 8 hr at 1000°C. Hot-pressing was carried out at 500°C and 50,000 psi when glass frit was added as a bonding agent and at 1175 to 1275°C and 1000 psi without any bonding agent. The rate of leaching of the activity from mica pellets was about 10^{-5} per cent per day and was considerably less when they were provided with an inactive coating.

Glassy products may be formed from Redox first-cycle waste by the addition of borate or of borate plus silicate followed by calcination.[7] Melting points range from 800 to 1200°C. The solubility of these materials has been measured as a function of moles of additive per equivalent of metallic cation in the waste. Melts obtained by adding borax or boric oxide alone disintegrated or dissolved completely in boiling water. Melts containing borax and sodium silicate had a minimum solubility of 1.3 per cent at an equivalence ratio of 2:1. Boric oxide with silica addition gave the lowest solubility, 0.06 per cent, at the same ratio.

The boric oxide—silica additions were also tried on Purex waste but did not give clear glassy melts such as were obtained with the Redox waste. Apparently the presence of aluminum and chromium in the Redox waste is important in melt formation with these particular additives. The phosphate and phosphate-borate systems continue to appear more attractive for use with Purex waste.

Calcination

The Hanford 8-in. radiant-heat calciner[11-13] was used for two long-duration runs, one for 18 and the other for 21 hr.[14] The feed was

formaldehyde-killed synthetic Purex waste. Build-up of solids on the walls of the column was no greater in the long-duration runs than in 1-hr runs, and increase in pressure drop across the off-gas filter was slight. Although operation of the radiant-heat spray calciner itself was uneventful, difficulty was encountered in the meltdown pot which was used to sinter the product. Faulty design and inadequate heating rate led to bridging with a plug of partially sintered powder. This bridging, although it was not related to the spray calciner proper, caused powder to back up and eventually shut down the first run.

The addition of borate to Redox and TBP-25 wastes has been previously shown to result in glassy melts. This was tried in the spray calciner with good results. Using TBP-25 waste and 1 mole of borate per metal equivalent, a dense vitreous glass was obtained. The density of the product was about 2 g/cm^3.

Better values than those previously reported have been obtained for off-gas de-entrainment. The de-entrainment factor from feed to noncondensable off-gas was 1.8×10^8, and the factor from feed to condensate was 1.5×10^4, both satisfactorily high. A summary report discussing the effect of various system parameters and giving an analysis of the heat transfer in radiant calcining became available during the quarter.[15]

At Idaho the completion schedule for the calciner facility has been delayed because of the steel strike. Therefore the originally scheduled turnover date of February 1960 will be deferred to June 1960.[16]

An Idaho summary report on the adsorption of ruthenium from calciner off-gas has been issued.[17] Calcined and commercially activated alumina, silica gel, two types of "molecular sieves," various stainless steels, and Marlex were examined in the temperature range 80 to 115°C as possible materials suitable for the removal of ruthenium from the off-gas of the Idaho Chemical Processing Plant (ICPP) aluminum nitrate waste calciner. Stainless-steel chips, calcined alumina, and both types of molecular sieves were rejected as unsuitable after preliminary tests. Stainless-steel screens and wool removed ruthenium adequately for short periods of time but soon reached their capacity for adsorbing this material. Marlex and commercial activated alumina proved unsatisfactory because they did not adapt themselves to a cyclic

process with liquid washing; furthermore, the latter adsorbent was attacked very severely both by raw calciner off-gas and by the aqueous reagents used for ruthenium removal.

Silica gel, which showed ruthenium decontamination factors of about 1000, appeared to be suitable for the purpose. It not only removed ruthenium satisfactorily from raw calciner off-gas, but its capacity for adsorbing ruthenium was large enough to allow infrequent bed cycling. It has been shown that the ruthenium can readily be removed from silica gel by washing with a small quantity (about 2 column volumes) of water. The portion of the ruthenium which was difficult to elute in this manner was about 10 per cent of the total on the column in cyclic tests and appeared to represent a strongly chemisorbed fraction. Neither the calciner off-gas contacting nor the elution appeared to be particularly detrimental to the gel, although precautions must be taken to prevent decrepitation during washing with water.

A proposed process at ORNL consists of first evaporating a waste to a very concentrated solution or slurry and then feeding to a stainless-steel cylindrical pot in which it is calcined to the oxides.[18] After being sealed, the pots would be removed from the furnace and stored in appropriate areas. The off-gas from the calciner, consisting principally of steam, nitrogen oxides, and fission products, must be decontaminated, possibly by scrubbing, before discharge to the environment. A concentrated solution of nitric acid and fission products would be recycled to the evaporator feed. Synthetic solutions representing wastes expected from processing of power reactor fuels have been characterized from the standpoint of their evaporation to dryness and the nature of the solids produced by calcination of the residues. Calcination studies were performed with 200-ml samples of radioactive wastes containing activities up to 2×10^{11} counts/(min)(ml) and with synthetic waste solutions in an electric furnace equipped with an 8-in.-diameter stainless-steel liner.

The behaviors of four simulated high-activity fuel processing solutions during evaporation and calcination were studied: Darex, Purex, Thorex, and TBP-25. Each waste was evaporated and then calcined to about 400°C in glass equipment. All solid residues were of high porosity, with volume reduction factors varying from 3 to 11 (Table IV-1). Nitrate recovery in the condensate ranged from 81 per cent to greater than 99 per

Table IV-1   EVAPORATION AND CALCINATION OF WASTES[18]

Waste	Consistency and color	Solid residue				Condensate, % of original	
		Density at 24°C, g/cm³	Porosity, %	Volume reduction factor	Nitrate, % of original	Volume	Weight
Darex (acidic)	Crumbly, dark brown	0.85	83	8	0.79	99.1	91.3
Purex (acidic)	Fairly hard, light brown	0.75	80	6.7	0.13	96.8	89.5
Thorex (acid-deficient)	Crumbly, off-white	0.31	92	11.4	4.0	101	97.5
TBP-25 (acidic)	Crumbly, off-white	0.56	86	3.3	16.8	95.7	84.5
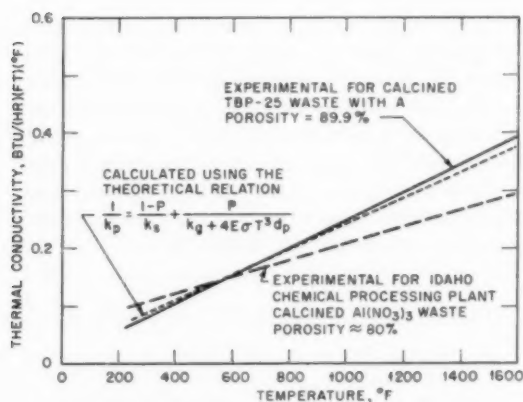
Figure 8 — Comparison of experimental and calculated thermal conductivity for a calcined TBP-25 waste.[19]

cent. In experiments on activity distribution during evaporation and calcination, greater than 99.94 per cent of the radioactivity remained with the residue.

Calculations have shown that none of the theoretical equations currently available for calculating the thermal conductivity of composite gas-solid materials fit exactly the experimental data obtained for a calcined TBP-25 waste. These equations calculate the thermal conductivity of such a two-phase material from the properties and volume fractions of the component substances.

The best fit thus far has been given by an equation of the form

$$\frac{1}{k_p} = \frac{1-P}{k_s} + \frac{P}{k_g + 4E\sigma T^3 d_p}$$

where k_p = the thermal conductivity of the granular porous body

k_g = the conductivity of the gas phase
k_s = the conductivity of the solid phase
E = the effective emissivity $(E/2 - E)$
σ = the radiation constant
T = the mean absolute temperature
d_p = the pore length
P = the porosity

The empirical fit obtained with this equation, using an effective mean pore length of 11.4 mm, is compared with the experimental results for a calcined TBP-25 waste and with the results obtained by P. N. Kelly at the ICPP on fluid-bed calcined aluminum nitrate waste in Fig. 8.

Final Disposal Methods

In the July 29, 1959, hearing on the disposal of low-level radioactive wastes at sea, held by the Special Subcommittee on Radiation of the Joint Committee on Atomic Energy, AEC General Manager A. R. Luedecke said that the AEC has thus far disposed of at sea the following quantities of radioactivity (at the time of disposal):[20]

1. In the Atlantic Ocean, about 8000 curies plus that in the reactor structure of the dismantled *Seawolf* prototype, which is estimated at 33,000 curies induced in stainless steel. The contained activity will be released to the sea through corrosion at an estimated rate of 2 to 3 curies a year. The major disposal areas are 230 miles and 150 miles southeast of Sandy Hook, both off the continental shelf at a depth greater than 1000 fathoms.

2. In the Pacific Ocean, about 14,000 curies at a site 48 miles west of the Golden Gate and about 60 curies at a site 53 miles west of Port

Vicente, Calif. Both sites are also at depths greater than 1000 fathoms.

Luedecke said that licensed private organizations and other government agencies have also disposed of a total of about 2600 curies in the
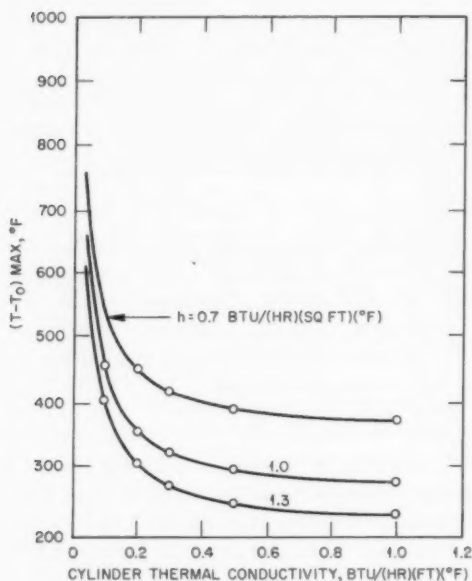

Figure 9—Maximum temperature rise in a cylinder of 1-year-decayed waste as a function of thermal conductivity and of the thermal convection coefficient in the air space of a salt medium. Q_0 = 700 Btu/(hr)(cu ft); cavity radius = 5 in. (references 18 and 22).
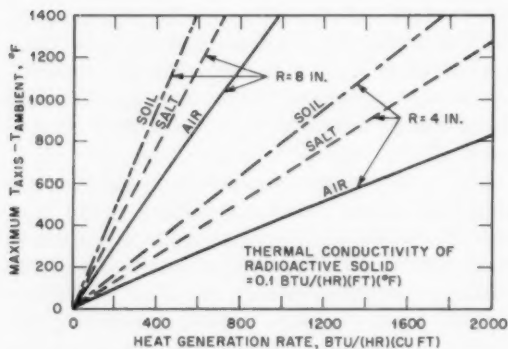

Figure 10—Maximum axial temperature rise of stored radioactive cylinders as a function of heat generation rate.[18,22] ——, storage in air with natural convection cooling. - - -, storage in an infinite salt medium with a 1-in. air space. — - —, storage in an infinite soil medium with a 1-in. air space.

Atlantic Ocean, 102 curies in the Pacific Ocean, and 10 curies in the Gulf of Mexico.

The estimated average cost for commercial sea disposal, at 1000 fathoms, of UCRL's radioactive waste from Berkeley and Livermore ranged from $7.48 to $8 per drum,[21] utilizing the cheaper of two concerns. The extra cost for disposal at 2000 fathoms instead of 1000 fathoms ranged from $0.33 per drum for a 3000-drum sea trip to $2.00 per drum for a 500-drum trip. The cost estimate for land burial of UCRL waste at HAPO, NRTS, and NTS ranged from $14.05 to $15.89 per drum if rail transportation were used, and from $14.90 to $19.25 per drum if through truck transportation were used.

Another set of temperature-rise calculations for deeply buried radioactive wastes has been made.[18,22] The model studied was an infinitely long cylinder of radioactive solid in an infinite solid medium with an air space between them. This model is pessimistic in that most other methods of storage would result in a lower temperature rise. The results are shown for various parameters in Figs. 9 and 10.

Separation of Specific Isotopes

Three alternates have been considered for recovering gross or mixed fission products from Purex waste.[23] These alternates are (1) gross fission-product recovery as an individual total program, (2) gross fission-product recovery as an incremental part of a waste solidification program, and (3) recovery of a mixture of Zr^{95} and Nb^{95} as an individual total program. Hanford costs for each case are summarized in Table IV-2. These estimates are derived from conceptual flow sheets and simple equipment layout studies. They are thus satisfactory for comparative purposes but are not firm in an absolute sense.

A peroxide–acetate precipitation process is under development for the separation of cerium from the trivalent rare earths.[7] The process is adaptable to operation in existing Purex plant equipment and has the advantage over previous processes that ruthenium volatilization is eliminated and that only noncorrosive reagents are used. The rare-earth double sulfate precipitate serves as starting material. This precipitate is dissolved, a hydrogen peroxide–sodium acetate solution is added and digested at 50°C, and the cerium peroxyacetate precipitate is separated

Table IV-2 COST ESTIMATES FOR RECOVERY OF FISSION PRODUCTS FROM WASTES[23]

	Gross fission products, total	Gross fission products, incremental	Mixed Zr–Nb[95]
Capital cost estimates:			
Process facility	$4,000,000	$2,000,000	$1,500,000
Cask inventory	1,500,000	1,500,000	250,000
Storage vault	4,000,000	4,000,000	1,800,000
Transferred capital charges:			
Building	$2,400,000		$2,400,000
Equipment	2,300,000		2,300,000
Annual charges:			
Operating cost	$2,400,000	$1,300,000	$1,400,000
Capital depreciation	1,800,000	700,000	1,050,000
Storage charge	800,000	800,000	360,000

by centrifugation. This precipitate is readily redissolved in nitric acid. The peroxide serves as oxidant to oxidize the cerium to the (IV) state, and the acetate serves both as precipitant and buffer. Accurate pH control (5.4 to 5.6) is essential. However, achievement of this is greatly facilitated by the buffer action of the acetate and should not present a serious plant operating problem. A reprecipitation may be required to free the cerium of all traces of trivalent rare earths.

One of the primary problems in the consideration of the present and future market for Cs^{137} is the pricing of this radioisotope. Based on present and probable future prices of Cs^{137} and Co^{60} for applications in which either radioisotope may be used, it is believed that Co^{60} will be preferred to Cs^{137} if the sources are to be sold and written off in about five years or less. On a rental basis (using an AEC write-off in 30 years), Cs^{137} will be preferred.[24]

Present markets for Cs^{137} sources are believed to exist in the following applications: teletherapy, industrial radiography, hospital radiosterilization of surgical supplies, commercial radiosterilization of bulk medical supplies, commercial sterilization of pharmaceuticals and medical specialties, promotion of chemical reactions, and research sources. The 1959 market is estimated to run from a minimum of 300,000 curies to a maximum of 8 million curies. It should be stressed that these markets can be expected to be realized only as a result of aggressive promotion, by both AEC and industry, of Cs^{137} and associated machines and equipment for using Cs^{137}.

A large future market for Cs^{137} is believed to exist primarily in the field of food processing with gamma radiation. Before this market becomes a reality, the Food and Drug Administration must approve the use of gamma radiation as a means of commercial processing of foods. Since sources for such applications will be in the multimegacurie range, the costs for the sources will be large and the pricing of Cs^{137} will be a most important consideration. It is believed[24] that by 1962 a market ranging from a minimum of 17 million curies to a maximum of 60 million curies will develop.

References

1. *Reactor Fuel Processing*, 2(2): (April 1959).
2. Hearings Before the Special Subcommittee on Radiation of the Joint Committee on Atomic Energy, Eighty-Sixth Congress of the United States, U. S. Government Printing Office, Washington 25, D. C., 1959.
3. Summary-Analysis of Hearings, January 28, 29, 30, February 2, 3, and July 29, 1959, Joint Committee on Atomic Energy, U. S. Government Printing Office, Washington 25, D. C., August 1959.
4. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., Vol. 6, No. 8, August 1959.
5. M. A. DeSesa, comp., Interim Report on Investigations into the Problem of Radioactive Pollution of Uranium Mill Effluents, WIN-101, Dec. 15, 1958. (Unclassified AEC report.)
6. W. E. Prout, Adsorption of Fission Products by Savannah River Plant Soil, DP-394, July 1959. (Unclassified AEC report.)
7. L. P. Bupp, Hanford Atomic Products Operation, Aug. 10, 1959. (Unpublished.)
8. C. Bernaud, The Industrial Problems Raised by the Processing of Radioactive Liquids: Some Specific Solutions Applied at Marcoule, A/CONF.15/P/1178, Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958.

9. W. A. Patrick, in Sanitary Engineering Aspects of the Atomic Energy Industry, TID-7517(Pt.Ib), p. 368, October 1956. (Unclassified AEC report.)
10. E. J. Evans and J. F. MacDonald, Atomic Energy of Canada, Ltd., March 1959. (Unpublished.)
11. *Reactor Fuel Processing*, 2(1): (January 1959).
12. *Reactor Fuel Processing*, 2(3): (July 1959).
13. *Reactor Fuel Processing*, 2(4): (October 1959).
14. L. P. Bupp, Hanford Atomic Products Operation, Sept. 10, 1959. (Unpublished.)
15. B. M. Johnson, Jr., Heat Transfer in Radiant-Heat Spray Calcination, HW-58641, Feb. 1, 1959. (Unclassified AEC report.)
16. Phillips Petroleum Co., private communication.
17. D. A. Hanson et al., The Adsorption of Ruthenium from Nitric Acid–Air Mixtures, IDO-14458, June 8, 1959. (Unclassified AEC report.)
18. F. L. Culler, Oak Ridge National Laboratory, September 1959. (Unpublished.)
19. Oak Ridge National Laboratory, June 1959. (Unpublished.)
20. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., Vol. 6, No. 9, September 1959.
21. Elmer Nielsen, Comparative Costs of Sea Disposal and Land Burial for the Radioactive Wastes of the Lawrence Radiation Laboratory, UCRL-8609, Jan. 21, 1959. (Unclassified AEC report.)
22. J. C. Bresee et al., Oak Ridge National Laboratory, March 1959. (Unpublished.)
23. E. A. Coppinger and B. F. Judson, Hanford Atomic Products Operation, Dec. 16, 1958. (Unpublished.)
24. L. E. Brownell, Consideration of the Present and Future Market for Cesium-137, HW-57670, Aug. 29, 1958. (Unclassified AEC report.)

Uranium Tetrafluoride

Moving Bed Reactor

The Moving Bed Reactor (MBR) process is one of several gas-solid contacting processes which have been evaluated as possible alternatives to the presently used screw reactor method for the production of uranium tetrafluoride.[1] The MBR process consists of (1) the agglomeration of uranium trioxide powder with water into pellet form, followed by setting or curing of the pellets by means of heat; and (2) successive pellet dehydration, reduction, and hydrofluorination by countercurrent gas contact as the pellets move by gravity at their normal settled bulk density down through a series of two reactors.

On the basis of preliminary engineering evaluations, the MBR process appeared to be economically superior to the existing method. The process was therefore subjected to study in a pilot-plant unit designed and installed at the Fernald site of the National Lead Company of Ohio. In the operation of the pilot-plant system, the major obstacles to successful operation were the inability to fabricate hydrated uranium trioxide pellets on a continuous basis and the difficulty of controlling reaction temperature by internal gas cooling during reduction and hydrofluorination. An interim economic evaluation[2] made in 1956, based on the assumption that the operating problems could be overcome, proved to be favorable to the MBR process when compared with a screw reactor system of like capacity.

A recently issued reevaluation[1] of the MBR process is based upon the operational information developed since the 1956 economic evaluation. The experimental operation of the pilot plant during 1956-1957 indicated that (1) uranium trioxide pellets can be produced by mixing and extrusion on a truly continuous basis;[3] (2) the temperature of the hydrogen reduction step can be controlled by feed gas dilution; and (3) the hydrofluorination reaction temperature

is amenable to control by the use of a hydrogen fluoride feed slightly greater than the stoichiometric requirement and by the use of a noncondensable gas for hydrogen fluoride dilution and sensible heat removal.

The design proposed in 1956 for an MBR system having a production capacity of 1140 tons of uranium per month has been revised. The proposed new system is shown in Fig. 11. Changes to the process effect an estimated saving of $140,000 in total investment costs due to firmer design of mixing and extrusion facilities and more efficient use of off-gases from the reactor system. Operating costs are slightly higher than those estimated previously because of the use of a higher excess of hydrogen fluoride.

The estimated investment and operating costs for the MBR plant are shown in Tables V-1 and V-2, respectively.[1] The total investment cost of $2,232,200 depends upon utilizing an existing building after some enlargement. The operating cost for the revised plant is $0.12 per pound of uranium processed. The cost of chemicals is the largest share of the total operating cost, representing 72 per cent of the total. The cost of anhydrous hydrogen fluoride represents nearly two-thirds of the total operating costs. Consequently, the operating costs of the MBR plant are largely dependent upon the cost of hydrogen fluoride.

Comparison of the operating and investment costs for this design with those of a previously designed plant indicates that the MBR process is still economically feasible. Further investigation is indicated to determine (1) the optimum method of pellet handling and curing after extrusion and (2) the measures required to eliminate gas or solids channeling within a reactor.

Photolytic Preparation

The photolytic preparation of uranium tetrafluoride utilizing solar energy has been demonstrated in India in laboratory-scale experiments.[4] When a saturated solution of uranyl

REACTOR SYSTEM EQUIPMENT LIST

1. Finished pellet storage hopper
2. Reduction reactor feed hopper
3. Reduction reactor
4. Cyclone
5. Cooler-condenser
6. Oxygen absorber
7. Dehydration gas heater
8. Reduction cyclone
9. Reduction gas heater
10. Salt cooling system (molten salt heat exchanger)
11. Hydrofluorination feed hopper (weigh scale hoppers)
12. Hydrofluorination reactor
13. Cyclone
14. Cooler-condenser
15. Gas-liquid disengaging tanks
16. Slurry recirculation tank
17. Lime hopper
18. Lime bucket elevator
19. Lime slurry make-up tank
20. Flocculation agent diss. tank
21. Lime slurry pumps
22. Thickened slurry pumps
23. Slurry thickener
24. AHF heater
25. UF$_4$ pellet product – receiving hopper
26. UF$_4$ powder storage hopper
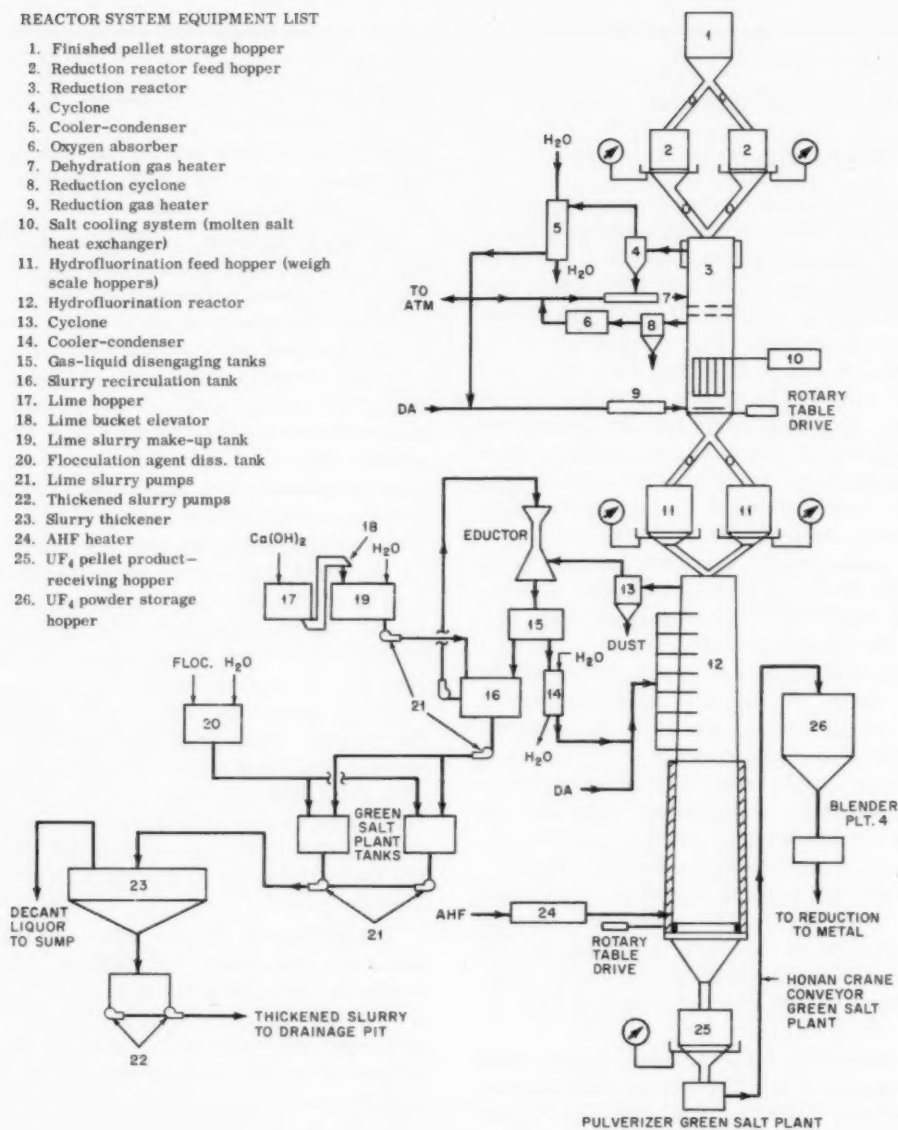
Figure 11 — Proposed reactor system, Moving Bed Reactor plant.[1]

Table V-1 SUMMARY OF INVESTMENT COSTS
(1958 EVALUATION) FOR THE MBR PLANT
AT A PRODUCTION RATE OF 1140 TONS
OF URANIUM PER MONTH[1]

Equipment cost:		
Pelleting equipment	$	161,400
Reactor equipment		362,600
Total	$	524,000
Piping cost (36% of equipment cost)		189,000
Instrumentation cost (20% of equipment cost)		105,000
Total material cost	$	818,000
Installation cost (43% of total material cost)		351,700
Construction supplies, equipment, supervision (20% of total material cost)		163,600
Process engineering and design (15% of total material cost)		122,700
Subtotal		$1,456,000
Overhead and fees (15% of subtotal)		218,400
Total installed cost		$1,674,400
Building costs:		
60-ft extension of height of green-salt plant (to 150 ft)	$	133,000
Addition of 24 by 36 by 34 ft to green-salt plant for housing of lime slurry system		44,000
Total cost		$1,851,400
Contingencies (10% of total cost)		185,000
Total investment cost		$2,036,400
Cost of auxiliary equipment now installed in green-salt plant and usable for MBR process		195,800
Total investment cost (for computing the annual maintenance cost)		$2,232,200

Table V-2 SUMMARY OF OPERATING COSTS FOR
THE MBR (1958 EVALUATION)[1]

(Basis: 1140 Tons of Uranium per Month)

		Per cent of total
Chemicals	$2,355,300	72
Utilities	120,200	4
Operating labor	302,300	9
Production and process control	112,200	3
Maintenance	106,600	3
General overhead	287,100	9
	$3,283,700	100

$$\text{Cost} = \frac{\$3,283,700 \text{ per year}}{27,390,000 \text{ lb of uranium per year}}$$

$$= \$0.12 \text{ per pound of uranium}$$

formate or nitrate in 38 to 40 per cent hydrofluoric acid (with half its volume being alcohol) was exposed to sunlight in a platinum basin, bright green uranium tetrafluoride began to appear in about 15 min. On further exposure, more of the compound formed and settled down. An advantage of this method is that no foreign substance is used for the reduction of the U(VI) to the U(IV) valency state. No data were reported on the percentage of uranium precipitated in these experiments.

Uranium Hexafluoride

Oxidation of Uranium Tetrafluoride

In the Fluorox process, uranium hexafluoride is prepared by oxidizing uranium tetrafluoride with dry oxygen or air at 700 to 850°C according to the reaction $2UF_4 + O_2 \rightarrow UF_6 + UO_2F_2$. The uranyl fluoride by-product is recycled back to the feed stream after hydrogen reduction and hydrofluorination. Development work aimed at the design and testing of a continuous fluidized-bed reactor for the oxidation reaction has been carried out at Oak Ridge.[5]

The all-Inconel reactor (Fig. 12) included a 4-in. fluidized-bed section, four porous metal filters for removing entrained solids and returning them to the bed, and a uranium tetrafluoride feeder to meter the feed into the bottom of the reactor. The off-gas system contained 8-in. cold traps for collecting the uranium hexafluoride product and a condensation pressure analyzer for measuring the uranium hexafluoride concentration in the reactor off-gas. The uranium tetrafluoride concentration in the fluidized bed was maintained below 10 per cent (remainder being uranyl fluoride) to decrease sintering and caking of the tetrafluoride above 800°C and to retard formation of uranium fluoride intermediates such as U_4F_{17}.

Runs were made with pure uranium tetrafluoride and both oxygen and air. More than 90 per cent of the theoretical amount of uranium hexafluoride was recovered from or measured in the reactor off-gas, the remainder being accounted for by various side reactions in which the hexafluoride reacted with water and uranium oxides introduced in the feed and with the metal walls of the reactor. The uranium tetrafluoride feed rate in these runs ranged from 1 to 1.6 kg/hr, and the total fluid-bed weight was approximately 6 kg. The only contaminant found in
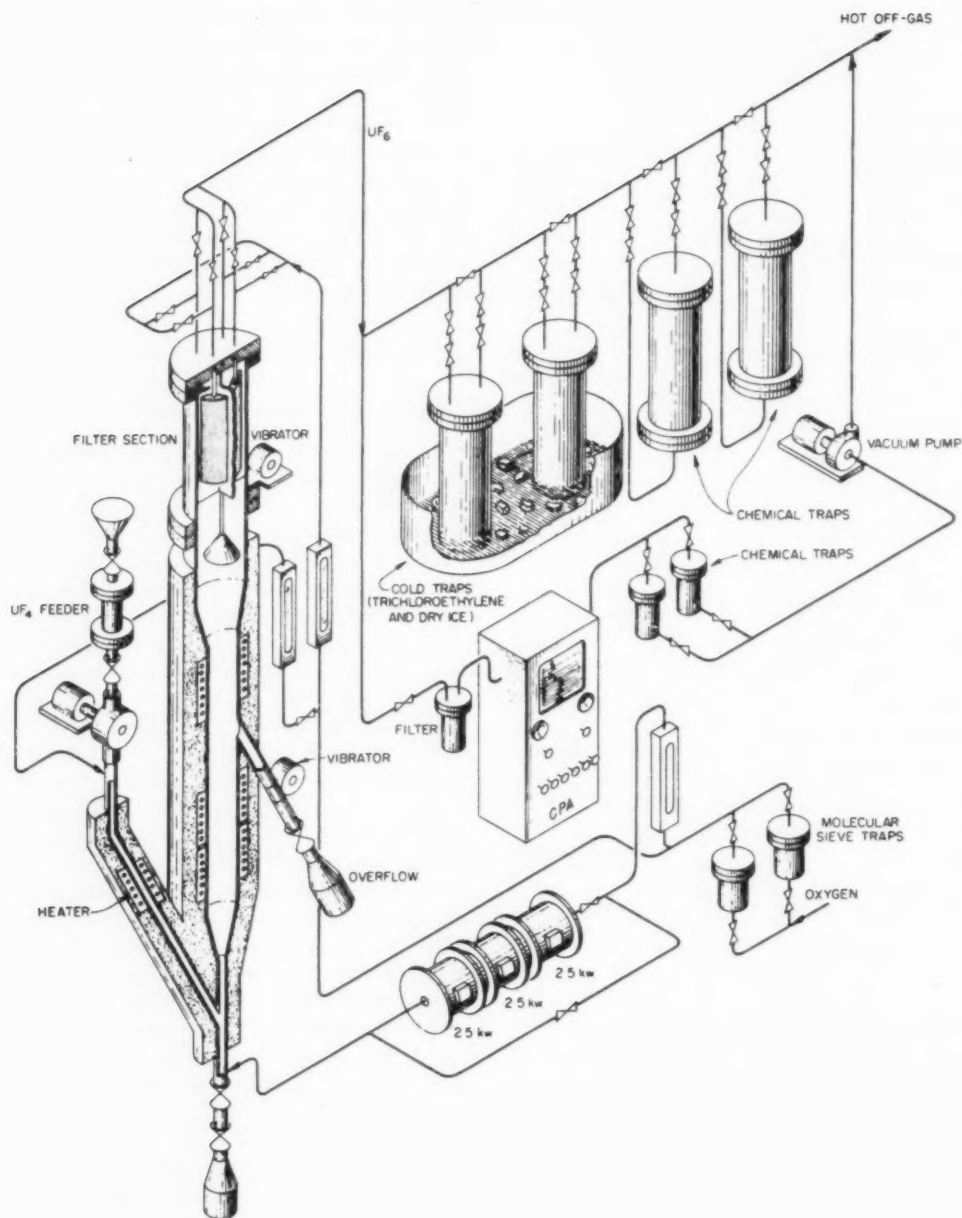
Figure 12 — Fluorox fluidized-bed reactor equipment.[5]

the hexafluoride product was hydrogen fluoride, which may be easily removed by volatilization.

Corrosion rates of 0.1 to 0.7 in. per year were measured in the fluidized-bed section of the reactor during experimental runs at 800 to 850°C with temperature excursions in some runs. If the temperature is kept below 850°C, corrosion can apparently be kept to the lower values. Corrosion in the gas phase of the reactor was insignificant.

In two runs made with crude uranium tetrafluoride (prepared from unpurified mill concen-

trate), corrosion of the Inconel reactor was prohibitive (~5 in. per year) at 700 to 725°C. Use of this type of feed (with subsequent purification of the uranium hexafluoride) may be possible if a suitable construction material can be found.

Since at least 50 per cent of the uranium from the uranium tetrafluoride oxidation results in uranyl fluoride, a complete process will require a method of recycling the uranyl fluoride. In a possible two-step recycle, the uranyl fluoride is reduced with hydrogen to uranium dioxide, which is hydrofluorinated to uranium tetrafluoride. The reaction of uranyl fluoride with hydrogen at 700 to 850°C was investigated in the laboratory.[6] The product was uranium dioxide, and no significant amount of uranium tetrafluoride was produced. The rate of the chemical reaction is sufficiently high for the desired application.

Recovery of Fluorine
from Uranium Hexafluoride

The storage of waste (depleted) uranium hexafluoride from gaseous diffusion plants costs several million dollars a year. An appreciable part of this cost comes from storage expense, principally storage cylinder costs. The contained uranium at present has little value, but the fluoride, if it could be made available as anhydrous hydrofluoric acid or elemental fluorine, has appreciable value. Since large amounts of both of these materials are needed for feed manufacture, a process that could supply them from waste uranium hexafluoride at costs below current values could save significant amounts of money. Additional savings would accrue from a reduction of storage costs if the uranium is changed to a form more economically handled.

Preliminary work on a process for the direct conversion of uranium hexafluoride to uranium dioxide by reaction with a steam-hydrogen mixture was described in the previous Review.[7] It appears possible to generate a high-assay hydrofluoric acid by this process. Other work has been performed to determine whether the electrolytic generation of fluorine from uranium hexafluoride is possible.[8] The major effort in this work was devoted to a search for a suitable electrolyte containing uranium hexafluoride or some easily derived similar compound. An extensive study of fluoride systems failed to reveal any system suitable for use as an electrolyte to generate fluorine from uranium tetrafluoride, uranium pentafluoride, or uranium

hexafluoride. Considerable effort was devoted to mixtures of potassium fluoride with either uranium hexafluoride or uranium pentafluoride. A mixture of potassium fluoride and uranium pentafluoride was found to have a solidus temperature of 500°F over the range 0.1 to 0.45 mole fraction potassium fluoride. Multicomponent mixtures containing uranium pentafluoride with potassium, lithium, and sodium fluorides were prepared, but the lowest solidus temperature found was 740°F.

Electrolysis experiments on these systems revealed that uranium pentafluoride reacts with the only known anode materials, carbon or graphite. Also, any reduction of the pentafluoride at the cathode results in formation of an insoluble uranium compound. In addition to the three requirements set for the electrolyte prior to this work (namely, that the melt should contain only fluoride anions, that it should contain no cations below uranium in the electromotive series, and that it should have a melting point not greater than 600°F), a fourth was added. Specifically, the uranium should be present in the quadrivalent state, or at least uranium in the quadrivalent state must have appreciable solubility in the melt. Such a material was not found in the course of this work.

A program to develop uses for depleted uranium has been started at Oak Ridge.[5] Nonreactor uses for uranium are insignificant at present, and fast reactors would use only a small fraction of the depleted uranium that will be produced in the next 40 years.

Recovery by Absorption-Distillation

Considerable work, primarily at the Oak Ridge Gaseous Diffusion Plant, has been done under quantitative recovery of uranium hexafluoride from a gaseous stream. A summary of this work was recently published.[9] Another recent report[10] describes in detail work performed on the absorption-distillation method which was done in 1952 and 1953. In this method, uranium hexafluoride was separated from nitrogen–uranium hexafluoride gas mixtures by continuous countercurrent absorption in liquid perfluorodimethylcyclohexane, C_8F_{16}. The solution of uranium hexafluoride in C_8F_{16} was separated by fractional distillation into an overhead of pure uranium hexafluoride and a bottom of pure C_8F_{16}.

A pilot plant with a capacity of 15,000 scf of feed gas per day was designed and built to study

the practicality of the above process. The process was not put into plant-scale operation.

Studies were made with uranium hexafluoride feed rates of 600 to 1900 lb/(hr)(sq ft) and concentrations of 29 to 56 mole % in nitrogen. The interconnected absorption-distillation system employing packed columns operated well on a continuous basis, and it was apparent that complete recovery of the uranium hexafluoride could be realized. The limiting gas and liquid rates agreed well with those predicted from standard correlations. For absorption, values of the height of a transfer unit ranged from 1.5 to 2.0 ft for $\frac{3}{8}$-in. aluminum Raschig rings, and for distillation the height of a theoretical plate at 50 per cent of flooding was 1.2 ft for $\frac{1}{2}$-in. Monel Raschig rings.

Uranium and Plutonium Metals

Reduction of Uranium Hexafluoride
to Metal

The reduction of uranium hexafluoride to uranium with sodium metal in the vapor phase is being studied.[5] The possible advantages of the process are continuous operation with a primary uranium feed material in a low-pressure reactor; lower reagent costs than those of the calcium or magnesium reduction process; and lower operating and capital costs than those of existing processes.

Uranium hexafluoride was reduced with sodium in a 6-in.-diameter reactor, which is essentially full scale for processing highly enriched uranium. The equipment included a system for vaporizing and metering uranium hexafluoride, a system for melting and metering sodium, and an Inconel reactor lined with graphite or a ceramic. The sodium flashed to vapor in the induction-heated reaction zone, and the reaction occurred in the vapor phase. Reduction products were collected in the bottom of the reaction chamber.

The two most serious problems have been the design of a suitable inlet nozzle for uranium hexafluoride and the development of a satisfactory liner to contain the reaction products (molten uranium and sodium fluoride) at temperatures as high as 1200°C. In some of the recent runs, a copper nozzle cooled internally with helium was used successfully, but consistently satisfactory operation has not been achieved.

Other inlet nozzle designs failed due to plugging or corrosion.

Magnesia and graphite were used as reactor liner materials, but these corroded, eroded, or cracked under the operating conditions. There is some evidence that liner disintegration may be due to the presence of liquid sodium, which penetrated pores and cracked the ceramic on flashing to vapor within the pores. After approximately a year of experimental work, a satisfactory liner material has not been developed.

In one run 88.3 per cent of the uranium introduced as hexafluoride was recovered as massive uranium metal with a purity of 99.6 per cent. There was also unconsolidated uranium metal in the slag and liner walls.

A series of batch experiments in which uranium hexafluoride and 100 per cent excess sodium were heated in sealed nickel reactors was performed to determine the yields and rates for the reactions

$$UF_6 + 2Na \rightarrow UF_4 + 2NaF$$

$$UF_4 + 4Na \rightarrow U + 4NaF$$

at 25 to 700°C. The rate for the first reaction was significant at 100°C. The second reaction did not become significant until the temperature exceeded 500°C. The second reaction was therefore considered to be the slower and limiting step. When a mixture of uranium tetrafluoride and sodium fluoride was reacted with sodium at 800°C, the reduction to metal was 80 per cent complete, but the uranium metal was pyrophoric and did not separate from the slag. After the sodium fluoride slag melting temperature was lowered by the addition of lithium fluoride in a similar experiment, reduction to metal was complete, the uranium crystals were large, and the uranium settled to the bottom of the reactor, thus indicating that operation above the melting point of the sodium fluoride slag (990°C) and the uranium metal (1130°C) is required for separation of slag from metal.

Laboratory experiments also showed that, when uranium metal was heated with sodium fluoride at 1200°C under vacuum, a reverse reaction occurred producing uranium tetrafluoride and sodium, which vaporized and condensed out of the reaction zone. It appears that a substantial excess of sodium (>50 per cent) will be necessary to ensure complete reduction to the metal.

Preparation of High-purity Uranium and Plutonium

Because the preparation of very high-purity uranium metal in massive form is important for research purposes, a program has been carried out at Los Alamos Scientific Laboratory to determine if uranium metal with very low concentrations of light elements could be produced by the bomb-reduction process.[11] The conventional process used at Los Alamos consists of reducing uranium tetrafluoride with calcium, using iodine as a booster, in a magnesium oxide crucible enclosed in a steel bomb. All ingredients for this process were examined as possible sources of light-element contamination.

The preparation of high-purity U_3O_8 as the starting material was accomplished by successive precipitations of uranium from uranyl nitrate solution, first as uranium peroxide and then as uranyl oxalate. Studies of equipment and materials of construction indicated that there was no advantage to the use of nonglass equipment for the precipitation operations. The reagents used in the precipitations contained significant amounts of impurities, but these were not transferred to the uranium oxide in the course of purification. The precipitated uranyl oxalate was calcined, reduced with electrolytic hydrogen, and then reacted with anhydrous hydrogen fluoride in a platinum boat.

The metallic calcium required for the bomb reduction was purified by distillation in a stainless-steel apparatus under argon atmosphere. Calcium metal containing less than 5 ppm magnesium and less than 25 ppm carbon was obtained in 35 to 40 per cent yield.

Calcium oxide was chosen as the material for the crucible. High-purity calcium oxide was prepared from analytical grade calcium chloride by precipitation of calcium oxalate which was then calcined to the oxide. Dry-pressed, sintered crucibles were fabricated and then heated to 900°C under vacuum to reduce the carbon content to less than 200 ppm.

By using the highly purified materials, bomb reductions were carried out in an argon atmosphere on a 250-g scale. The as-reduced uranium metal contained, on the average, less than the following amounts of light-element impurities (in ppm): Li, 0.1; Be, 0.1; B, 0.1; C, 25; O, 70; Na, 1; Mg, 3; Al, 2; and Si, 7. Other impurities for which the metal was examined averaged (in ppm): Ca, <10; V, <10; Cr, 2; Mn, 6; Fe, 50; Co, <5; Ni, 8; and Cu, 1.

Nearly the same procedure was followed for the preparation of high-purity plutonium metal, except that initial purification of the plutonium was obtained by two successive peroxide precipitations. The total detectable impurities in the alpha-phase plutonium metal produced varied from 94 to 276 ppm.[12]

Uranium Recovery from Slag

The processing of slag resulting from the magnesium reduction of uranium tetrafluoride currently involves an acid leach to separate the uranium from the magnesium fluoride. Purification of the uranium is accomplished by either of two methods. At the Fernald, Ohio, plant the acid-leach step is followed by precipitation and calcination to produce a uranium phosphate compound. This phosphate is then processed to uranium trioxide, which is fed to the green-salt plant for conversion to uranium tetrafluoride. At the Y-12 Plant (Oak Ridge) the sulfuric acid–leach step is followed by pH adjustment, filtration, and purification in a Higgins ion-exchange column.

As an alternative method of purification, solvent extraction has been investigated at both Oak Ridge[13] and Fernald.[14] The solvents studied were those used commercially for recovery of uranium from ore leach solutions in some uranium mills. One process uses certain long-chain amines, such as Rohm and Haas LA-1, dissolved in kerosene; this solvent extracts uranium by anion exchange analogous to resins. Dilute hydrochloric acid can be used to strip the uranium from the solvent. Another process uses di-2-ethylhexyl phosphoric acid (D2EHPA) in kerosene, usually with added tributyl phosphate. Uranium can be stripped with solutions of ammonium carbonate.

For application to slag leach liquor or slurry, the choice between the two types of solvents is not clear-cut. Satisfactory results were obtained in bench-scale mixer-settler runs using the amine solvent at Fernald and the D2EHPA solvent at Oak Ridge. The amines extract uranium more rapidly and are more selective for uranium, whereas D2EHPA has a higher extraction coefficient and permits good separation of uranium from sulfate.

Other experimental work was performed at Fernald to demonstrate the aqueous precipitation of metal-grade uranium tetrafluoride from the solvent-extraction product stream by the Winlo process. The unique feature of this process is the reduction and precipitation of uranium in fluoride solution by sulfur dioxide gas in the presence of cupric chloride complex ion as catalyst.[15] A flow sheet for recovery of uranium from slag by amine extraction and uranium tetrafluoride precipitation was developed, and metal-grade tetrafluoride was produced in small-scale tests.

In considering the conversion of the present Metals Recovery Plant at Fernald, it was thought that the use of the existing uranium ammonium phosphate precipitation process, in conjunction with the Winlo process to produce uranium tetrafluoride, would permit the earliest possible conversion date. Accordingly, laboratory experiments were performed which determined the amount of purification obtained by this process and the optimum precipitation conditions from the standpoint of uranium tetrafluoride purity and precipitation time. Metal-grade tetrafluoride was precipitated from hydrochloric acid solutions of uranium phosphate produced in the Metals Recovery Plant. In addition, all the high-grade black oxide (U_3O_8) scrap resulting from the burning of chips, turnings, sludges, etc., was found to be of sufficient purity to produce metal-grade tetrafluoride by hydrochloric acid dissolution and aqueous precipitation by the Winlo process. In pilot-scale studies of the precipitation step, no problems were encountered which would indicate trouble in further scale-up. Kel-F lined steel was unsatisfactory as a material of construction, but Karbate and rubber-lined steel appear promising.

Development work directed toward improving the economics of the acid-leaching step in the Metals Recovery Plant has also been carried out.[16] The hydrochloric acid used in the leaching operation must be partially neutralized to recover the uranium and must be totally neutralized before disposal. Because neutralization of the excess acid represented an economic burden, a program was initiated to develop process changes which would provide more favorable acid economy. As a result of modifications developed from laboratory data and demonstrated in the plant, the conservation of acid and hydroxide values was effected by acid recycle and high-pulp-density leaching techniques. Substitution of sulfuric acid for hydrochloric acid was also investigated and found to offer potential additional savings, but the change to sulfuric acid on a plant scale was deferred because of the additional capital equipment required.

References

1. D. J. Loudin, Evaluation of the Moving Bed Reactor Process for the Production of Uranium Tetrafluoride: Termination Report, NLCO-722, Feb. 12, 1958. (Unclassified AEC report.)
2. H. F. Muhlhauser and D. J. Loudin, Interim Economic Evaluation of the Moving Bed Reactor Process for Production of Uranium Tetrafluoride, NLCO-646, Aug. 2, 1956. (Confidential AEC report.)
3. P. W. Henline, E. W. Mautz, and E. J. Walter, Production of Porous Pellets of Hydrated Orange Oxide, NLCO-718, July 1, 1957. (Unclassified AEC report.)
4. D. Patnaik and B. Sahoo, The Photolytic Preparation of Uranium Tetrafluoride, *Proceedings of the Indian Academy of Sciences*, 49(A): 200-202 (April 1959).
5. Oak Ridge National Laboratory, September 1959. (Unpublished.)
6. L. M. Ferris and R. P. Gardner, Recycle of UO_2F_2 in the Fluorox Process: Reaction of UO_2F_2 with Hydrogen, ORNL-2690, July 9, 1959. (Unclassified AEC report.)
7. *Reactor Fuel Processing*, 2(4): (October 1959).
8. W. R. Rossmassler, R. L. Harris, and T. J. Mayo, On the Electrolytic Generation of Fluorine from Uranium Hexafluoride, KY-287, May 1, 1959. (Confidential AEC report.)
9. S. H. Smiley et al., Quantitative Recovery of Uranium Hexafluoride from a Process Gas Stream: Evaluation of Methods, *Industrial and Engineering Chemistry*, 51: 191-196 (1959).
10. R. A. Ebel et al., Recovery of Uranium Hexafluoride from a Process Gas Stream by Absorption-Distillation Techniques Employing a Liquid Fluorocarbon Medium, K-1366, Oct. 15, 1959. (Unclassified AEC report.)
11. R. W. Kewish et al., The Preparation of High-purity Uranium Metal by the Bomb Reduction of Uranium Tetrafluoride with Calcium, *Transactions of the Metallurgical Society of AIME*, 215: 425-529 (June 1959).
12. K. W. R. Johnson, The Preparation of High-purity Plutonium Metal, *Journal of Inorganic & Nuclear Chemistry*, 9: 200-203 (March 1959).
13. A. D. Ryon and F. L. Daley, Solvent Extraction of Uranium from Reduction Slag Slurry, ORNL-2744, July 28, 1959. (Unclassified AEC report.)
14. E. O. Rutenkroger and J. H. Cavendish, The

Preparation of Metal Grade UF$_4$ from Scrap by the Winlo Process, NLCO-788, June 8, 1959. (Unclassified AEC report.)

15. *Reactor Fuel Processing*, 2(2): (April 1959).

16. A. B. Kreuzmann and E. O. Rutenkroger, Investigation of Hydrometallurgical System Acid Leaching Media, NLCO-781, Oct. 27, 1958. (Unclassified AEC report.)

NUCLEAR SCIENCE ABSTRACTS
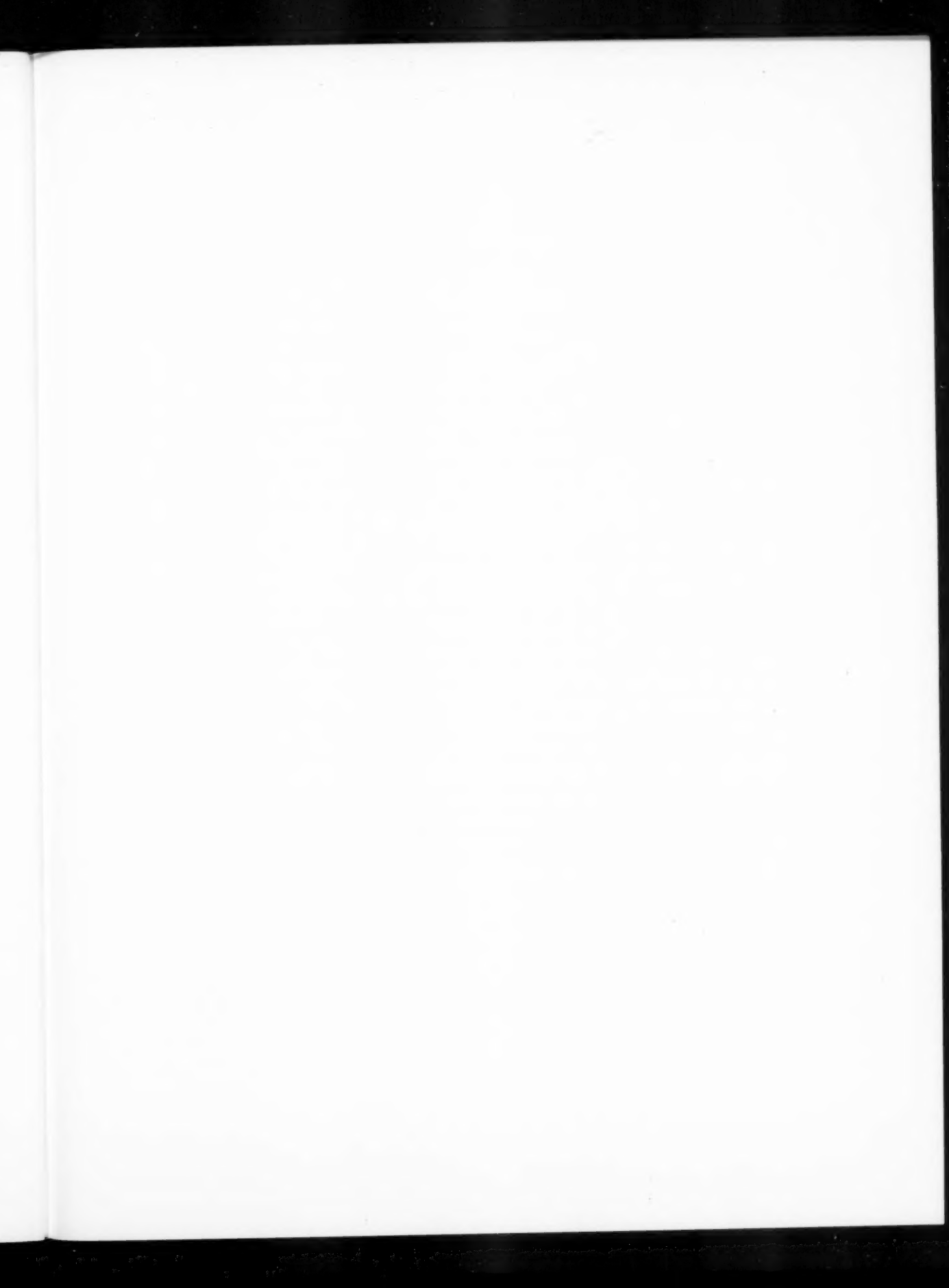
The U. S. Atomic Energy Commission, Technical Information Service, publishes *Nuclear Science Abstracts (NSA)*, a semimonthly journal containing abstracts of the literature of nuclear science and engineering.

NSA covers (1) research reports of the U. S. Atomic Energy Commission and its contractors; (2) research reports of government agencies, universities, and industrial research organizations on a world-wide basis; and (3) translations, patents, books, and articles appearing in technical and scientific journals.

Complete indexes covering subject, author, source, and report number are included in each issue. These are cumulated quarterly, semiannually, and annually providing a detailed and convenient key to the literature.

Availability of NSA

SALE *NSA* is available on subscription from the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C., at $18.00 per year for the semimonthly abstract issues and $15.00 per year for the four cumulated-index issues. Subscriptions are postpaid within the United States, its Territories, Canada, Mexico, and all Central and South American countries, except Argentina, Brazil, British and French Guiana, Surinam, and British Honduras. Subscribers in these Central and South American countries, and in all other countries throughout the world, should remit $22.50 per year for subscriptions to semimonthly abstract issues and $17.50 per year for the four cumulated-index issues.

EXCHANGE *NSA* is also available on an exchange basis to universities, research institutions, industrial firms, and publishers of scientific information. Inquiries should be directed to the Technical Information Service Extension, U. S. Atomic Energy Commission, P. O. Box 62, Oak Ridge, Tennessee.

REACTOR FUEL PROCESSING may be purchased ($2.00 per year, $0.55 per issue) from the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C. The use of the coupon below will facilitate the handling of your order.

POSTAGE AND REMITTANCE: Postpaid within the United States, Canada, Mexico, and all Central and South American countries except as hereinafter noted. Add $0.50 per year, or $0.15 per single issue, for postage to all other countries, including Argentina, Brazil, British and French Guiana, Surinam, and British Honduras. Payment should be by check, money order, or document coupons, and MUST accompany order. Remittances from foreign countries should be made by international money order, or draft on an American bank, payable to the Superintendent of Documents, or by UNESCO book coupons.

order form

SUPERINTENDENT OF DOCUMENTS
U. S. GOVERNMENT PRINTING OFFICE
WASHINGTON 25, D. C.

Enclosed:
    document coupons ☐   check ☐   money order ☐

Charge to Superintendent of Documents No. _ _ _ _ _ _ _ _ _

Please send me a one-year subscription to

REACTOR FUEL PROCESSING
($2.00 a year; $0.55 per issue.)

SUPERINTENDENT OF DOCUMENTS
U. S. GOVERNMENT PRINTING OFFICE
WASHINGTON 25, D. C.

(Print clearly)

Name _

Street _

City _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ Zone _ _ _ _ State _ _ _ _ _ _ _